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ENTS OF CHEMISTRY

ELEMENTS OF CHEMISTRY.

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Second Edition

ELEMENTS OF CHEMISTRY,

INCLUDING THE

RECENT DISCOVERIES AND DOCTRINES OF THE SCIENCE.

BY THE LATE

EDWARD TURNER, M.D.

SIXTH EDITION, ENLARGED AND REVISED.

BY

JUSTUS LIEBIG,

PROFESSOR OF CHEMISTRY IN THE UNIVERSITY OF GIESSEN;

AND

WILTON G. TURNER.



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ADVERTISEMENT.

IN consequence of the death of the Author, it became necessary to arrange for the preparation of the present and future editions of this work. The Publishers hope that the engagements into which they have entered will ensure to the "Elements of Chemistry" that position which it has hitherto enjoyed. The conduct of the work has been entrusted to Professor Liebig and Mr. Wilton G. Turner.

The department of Inorganic Chemistry has been prepared by Mr. Turner. The description of the Imponderable Agents was left nearly ready for the press by the Author, and the only additions necessary were the insertion of a few recent discoveries. In the remainder of this section, the Editor has endeavoured to effect the improvements which he was aware had been contemplated by his brother. He has, consequently, treated of the Elements and their Compounds, under the three heads of History, Preparation, and Properties. An arrangement which, it is hoped, will not only increase the utility of the work as a book of reference, but will add to the clearness of its descriptions. The old chapter on Crystallography was formed on the views of Haüy; it has been re-written, to suit the present state of the science.

The department of Organic Chemistry requires to be entirely re-written, owing to the many new facts which have been discovered since the publication of the last edition. This Professor Liebig has kindly undertaken. In the volume about to be presented to the public will therefore be developed, for the first time, the views of this distinguished chemist on that department of the science to which he has devoted his particular attention. A departure from the mode of publication originally announced has consequently been occasioned. The work will now consist of Three Parts. Part II., containing the Metals and Salts, will be ready by the first week in November, and with Part I. will embrace that portion of the subject required for Lectures previous to April. Part III., consisting of Organic Chemistry, will be published early in 1838. In consequence of the arrangement adopted by Professor Liebig, it has become necessary to transfer to his section the description of several substances formerly treated under Inorganic Chemistry.

In a Preface by the Editors, which will accompany the Third Part, will be given a more particular account of the changes adopted in this edition. An Appendix will be added, containing any discoveries that may have been made during the publication of the work.

28, Upper Gower Street,
September 7, 1837.

PREFACE

TO

THE FIRST EDITION.

THE following pages comprehend a condensed view of the present state of Chemical Science. The chief purpose of the work is to make the Student intimately acquainted with the theory, at the same time that he is acquiring a knowledge of the facts, of Chemistry; so that, by the establishment of fixed principles, the details may more easily be impressed on the memory, and excite an interest which they would not otherwise possess. Every one who is acquainted with modern Chemistry, will admit that the study of the Laws of Combination is fitted in a peculiar manner for promoting these objects; and hence I have treated at length of the Atomic Theory, and the subjects connected with it, at an early part of the volume.

To this arrangement, I am aware, it may be objected, that many of the facts adduced as illustrations must necessarily be unknown to the beginner. I do not anticipate, however, any serious inconvenience from this source; on the contrary, some experience in teaching the theoretical and practical details of the Science gives me reason to think that the disadvantages of my plan will be very far outweighed by its advantages. I may observe, indeed, that this work is chiefly designed for persons who have

either attended, or are attending, Lectures on Chemistry ; and, to such readers, the objection to which I allude does not apply.

In the composition of this work, I have had recourse, as far as possible, to original sources of information ; but I have also derived much assistance from the Elements of Sir H. Davy, and Dr. Henry ; from the Systems of M. Thenard and the late Dr. Murray ; and from the System and First Principles of Dr. Thomson. I should also add, that the materials of the Small Treatise, published about eighteen months ago, on the Laws of Combination and the Atomic Theory, are, with slight modifications, incorporated in the present Volume.

This Treatise, however, is not to be viewed in the light of a mere compilation. In the purely practical parts of the Work, for example, in describing processes, in giving the tests for demonstrating the presence of substances, and in explaining the rules for conducting Chemical Analysis, I have in general merely stated in writing what I am in the habit of practising in the Laboratory. It is likewise proper to mention, that in detailing the experimental results obtained by other chemists, I have in many instances verified them by my own observation ; and when treating of the obscure or disputed parts of the Science, I have taken pains to render the former clear, and to distinguish in the latter what is ascertained from what is still undetermined.

EDINBURGH, Feb. 1, 1827.

P R E F A C E

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THE FIFTH EDITION.

IN preparing a Fifth Edition of these Elements, I have not lost sight of the plan on which the Work was originally framed. Its object is still, without entering minutely into the details of processes and experiments, to present a concise and connected view of the facts and theories of Chemistry. It has been found impossible, so numerous are the cultivators of this science, and so rapid its progress, to avoid numerous changes and additions. These have necessarily been interwoven with the texture of the volume, and it would be useless, were it practicable, to enter into an exact enumeration of them; but it may be convenient to some readers that the more important variations from former editions should be specified.

In the first section there are but few changes, and those relate chiefly to Radiant Heat. In that on Light, a summary of the laws of reflection and refraction, agreeably to the wishes of some of my pupils, has been supplied. The article on Electricity has been almost entirely recomposed; and, owing to the kindness of Mr. Snow Harris, I have been enabled to embody many results of his late researches, prior to their appearance in a printed form before the public. I have to acknowledge a similar kindness in Mr. Faraday, whose discoveries in Galvanism

have compelled me to remodel the whole of the fourth section. To procure all the facts required for that purpose, I have been obliged to delay writing the section on Galvanism until the other parts of the volume were completed. This will account for the intercalation of a leaf at page 154, and for the labours of Mr. Faraday not being referred to in other portions of the volume, which, though placed after the fourth section, were, in fact, printed some weeks earlier.

A few changes have been made in the section on the Laws of Combination, where will also be found a description of the mode of employing Symbols in Chemistry. I ventured in the last edition to introduce chemical symbols as an organ of instruction, and subsequent experience has afforded such convincing evidence of their value in this point of view, that I cannot too earnestly urge the chemical student to employ them at an early period of his studies. The present state of Chemistry renders the use of abbreviated or symbolic language almost unavoidable; and the question now is, not so much whether they shall be used, as whether they shall be generally understood. To ensure this, it is essential that a uniform system be adopted; and I have hence felt the necessity of strictly conforming to the method introduced by Berzelius and adopted on the Continent. The Tables which have been given in the sections of the second and third parts, with the primary view of showing Analogies of chemical constitution, will serve the useful secondary purpose of supplying a guide to the employment of symbols. By reference to them, the student will see the meaning of any symbols he may meet with in the text.

The large number of compounds which have gradually accumulated, possessing the aspect and general characters of salts, and yet not composed of acids and alkalies in the general acceptation of these terms, have been arranged as separate orders of a large class of saline substances, which are inseparably allied by analogy of composition. But in associating substances naturally connected, I have abstained from violating any established usages in terminology. Changes in chemical nomenclature should be attempted rather by a community of chemists than by an individual; and if the labours of the Committee which the British Association has appointed for promoting uniformity in the use of symbols shall be attended with that success which its proposer anticipates, a like task in reference to chemical nomenclature may well be imposed on the same Committee. For the greater part of our knowledge of the compounds here referred to, we are indebted to Berzelius, and the principal facts concerning them are drawn from his writings.

Owing to the activity displayed in organic analysis by several Continental chemists, especially by Liebig and Dumas, the necessary additions and changes in the Third Part have been very considerable. I am conscious that the arrangement of organic substances stands in need of revision; but it is easy to trace defects in any given arrangement on such a subject, and very difficult to fix on one which shall not be liable to equal objection. Considering facility of consultation of far more importance to the reader than critical propriety of classification, I have thought it right for the present to describe organic compounds nearly in the same order as in former editions.

In the Appendix will be found an interesting commu-

nication, kindly sent me by Mr. Graham, on the nature of certain hydrated salts and peroxides, and on phosphuretted hydrogen. It likewise contains other notices which either reached me too late for insertion in the body of the work, or were accidentally omitted.

I have again to express my thanks to Dr. Franklin Bache, Editor of the American Edition, for several valuable suggestions.

LONDON, Nov. 1, 1834.

INTRODUCTION.

MATERIAL substances are endowed with two kinds of properties, physical and chemical ; and the study of the phenomena occasioned by them has given rise to two corresponding branches of knowledge, *Natural Philosophy* and *Chemistry*.

The physical properties are either general or secondary. The general are so called because they are common to all bodies ; the secondary, from being observable in some substances only. Among the general may be enumerated extension, impenetrability, mobility, extreme divisibility, gravitation, porosity, and indestructibility.

Extension is the property of occupying a certain portion of space : a substance is said to be *extended* when it possesses length, breadth, and thickness. By *impenetrability* is meant that no two portions of matter can occupy the same space at the same moment. Every thing that possesses extension and impenetrability is matter.

Matter, though susceptible of *rest and motion*, has no inherent power either of beginning to move when at rest, or of arresting its progress when in motion. Its indifference to either state has been expressed by the term *vis inertiae*, as if it depended on some peculiar force resident in matter, whereas it arises from matter being absolutely passive, and thereby subject to the influence of every force which is capable of acting upon it.

Matter is *divisible* to an extreme degree of minuteness. A grain of gold may be so extended by hammering that it will cover 50 square inches of surface, and contain two millions of visible points ; and the gold which covers the silver wire, used in making gold lace, is spread over a surface twelve times as great. A grain of iron, dissolved in nitro-hydrochloric acid, and mixed with 3187

pints of water, will be diffused through the whole mass : by means of the ferro-cyanuret of potassium, which strikes an uniform blue tint, some portion of iron may be detected in every part of the liquid. The grain of iron is hence inferred to have been divided into rather more than 24 millions of parts ; and if the dilution were carried still further, the diffusion of iron through the whole liquid might be proved by concentrating any portion of it by evaporation, and detecting the metal by its appropriate tests.

A keen controversy existed at one time concerning the divisibility of matter, some philosophers affirming it to be infinitely divisible, while others maintained an opposite opinion. Owing to the imperfection of our senses the question cannot be determined by direct experiment, because matter certainly continues to be divisible long after it has ceased to be an object of sense. The decision, if effected at all, can only be accomplished indirectly, as an inference from other phenomena. In favour of the former view it was urged, on mathematical grounds, that a surface admits of division without limit ; and that to whatever degree matter is divided, it may still be conceived, in possessing extension and surface, to be susceptible of still further division. Plausible, however, as this mode of reasoning may appear, the opposite opinion is daily becoming more general. It is now commonly believed that matter consists of ultimate particles or molecules, which may indeed be conceived to be divisible, but which by hypothesis are assumed to be infinitely hard and impenetrable, and on that account to be incapable of division. These ultimate particles have received the appellation of *atoms*, (from the privative α and $\tau\epsilon\mu\nu\nu\alpha\iota$ to cut,) as expressive of their nature. The arguments adduced in support of this opinion are principally drawn from the phenomena of chemistry, and from the relations which have been observed to exist between the composition and form of crystallized bodies. These subjects will be considered hereafter: it will now suffice to state, in order to show the nature of the argument, that the supposed existence of atoms accounts for numerous facts, which cannot be satisfactorily explained on any other principle.

All bodies descend in straight lines towards the centre of the earth, when left at liberty at a distance from its surface. The power which produces this effect is termed *gravity*, *attraction of gravitation*, or *terrestrial attraction* ; and the force required to separate a body from the surface of the earth, or prevent it from descending towards it, is called its *weight*. Every particle of matter is equally

affected by gravity ; and therefore the weight of any body will be proportionate to the number of ponderable particles which it contains.

The minute particles of which bodies consist, are disposed in such a manner as to leave certain intervals or spaces between them, and this arrangement is called *porosity*. These interstices may sometimes be seen by the naked eye, and frequently by the aid of glasses ; but were they wholly invisible, it would still be certain that they exist. All substances, even the most compact, may be diminished in bulk either by mechanical force or a reduction of temperature. It hence follows that their particles must touch each other at a very few points only, if at all ; for if their contact were so perfect as to leave no interstitial spaces, then would it be impossible to diminish the dimensions of a body, because matter is incompressible and cannot yield.—When therefore a body expands, the distance between its particles is increased ; and, conversely, when it contracts or diminishes in size, its particles approach each other.

By *indestructibility* is meant, that, according to the present laws of nature, matter never ceases to exist. This statement seems at first view contrary to fact. Water and volatile substances are dissipated by heat, and lost ; coals and wood are consumed in the fire, and disappear. But in these and all similar phenomena not a particle of matter is annihilated. The apparent destruction is owing merely to a change of form or composition ; for the same material particles, after having undergone any number of such changes, may still be proved to possess the characteristic properties of matter.

The *secondary* properties of matter are opacity, transparency, softness, hardness, elasticity, colour, density, solidity, fluidity, and others of a like nature. Several of these properties, especially those last specified, depend on the relative intensity of two opposite forces—cohesion and repulsion. It is inferred, from the divisibility of matter, that the substance of solids and liquids is made up of an infinity of minute particles adhering together so as to constitute larger masses ; and that the mutual adhesion of these particles is owing to a power of reciprocal attraction. This force is called *cohesion*, *cohesive attraction*, or the *attraction of aggregation*, in order to distinguish it from terrestrial attraction. Gravity is exerted between different masses of matter, and acts at sensible and frequently at very great distances ; while cohesion exerts its influence only at insensible and infinitely small distances. It enables

similar molecules to cohere, and tends to keep them in that condition. It is best exemplified by the force required to separate a hard body, such as iron or marble, into smaller fragments; or by the weight which twine or metallic wire will support without breaking.

The tendency of cohesion is manifestly to bring the ultimate particles of bodies into immediate contact; and such would be the result of its influence, were it not counteracted by an opposing force, a principle of repulsion, which prevents their approximation. It is a general opinion among philosophers, supported by very strong facts, that this repulsion is owing to the agency of heat, which is somehow attached to the elementary molecules of matter, causing them to repel one another. Material substances are therefore subject to the action of two contrary and antagonizing forces, one tending to separate their particles, the other to bring them into closer proximity. The form of bodies, as to solidity and fluidity, is determined by the relative intensity of these powers. Cohesion predominates in solids, in consequence of which their particles are prevented from moving freely on one another. The particles of a fluid, on the contrary, are far less influenced by cohesion, being free to move on each other with very slight friction. Fluids are of two kinds; elastic fluids or æriform substances, and inelastic fluids or liquids. Cohesion seems wholly wanting in the former; they yield readily to compression, and expand when the pressure is removed; indeed, the space they occupy is chiefly determined by the force which compresses them. The latter, on the contrary, do not yield perceptibly to ordinary degrees of compression, nor does an appreciable dilatation ensue from the removal of pressure, the tendency of repulsion being in them counterbalanced by cohesion.

Matter is subject to another kind of attraction different from those yet mentioned, termed *chemical attraction* or *affinity*. Like cohesion it acts only at insensible distances, and thus differs entirely from gravity. It is distinguished from cohesion by being exerted between dissimilar particles only, while the attraction of cohesion unites similar particles. Thus, a piece of marble is an aggregate of smaller portions attached to each other by cohesion, and the parts so attached are called *integrant* particles; each of which, however minute, being as perfect marble as the mass itself. But the integrant particles consist of two substances, lime and carbonic acid, which are different from one another as well as from

marble, and are united by chemical attraction. They are the *component* or *constituent* parts of marble. The integrant particles of a body are therefore aggregated together by cohesion; the component parts are united by affinity.

The chemical properties of bodies are owing to affinity, and every chemical phenomenon is produced by the operation of this principle. Though it extends its influence over all substances, yet it affects them in very different degrees, and is subject to peculiar modifications. Of three bodies, A, B, and C, it is often found that B and C evince no affinity for one another, and therefore do not combine; that A, on the contrary, has an affinity for B and C, and can enter into separate combination with each of them; but that A has a greater attraction for C than for B, so that if we bring C in contact with a compound of A and B, A will quit B and unite by preference with C. The union of two substances is called *combination*; and its result is the formation of a new body endowed with properties peculiar to itself, and different from those of its constituents. The change is frequently attended by the destruction of a previously existing compound, and in that case *decomposition* is said to be effected.

The operation of chemical attraction, as thus explained, lays open a wide and interesting field of inquiry. One may study, for example, the affinity existing between different substances; an attempt may be made to discover the proportions in which they unite; and finally, after collecting and arranging an extensive series of insulated facts, general conclusions may be deduced from them. Hence chemistry may be defined the science, the object of which is to examine the relations that affinity establishes between bodies, ascertain with precision the nature and constitution of the compounds it produces, and determine the laws by which its action is regulated.

Material substances are divided by the chemist into simple and compound. He regards those bodies as compound, which may be resolved into two or more kinds of ponderable matter; those as simple or elementary, which contain but one. The number of the latter amounts only to fifty-four; and of these, agreeably to our present knowledge, all the bodies in the earth consist. The list, a few years ago, was somewhat different from what it is at present; for the acquisition of improved methods of analysis has enabled chemists to demonstrate that some substances, which were once supposed to be simple, are in reality compound; and it is probable

that a similar fate awaits some of those which are at present regarded as simple.

The composition of a body may be determined in two ways, analytically or synthetically. By analysis, the elements of a compound are separated from one another, as when water is resolved by the agency of galvanism into oxygen and hydrogen; by synthesis they are made to combine, as when oxygen and hydrogen unite by the electric spark, and generate a portion of water. Each of these kinds of proof is satisfactory; but when they are conjoined—when water is resolved into its elements, and then reproduced by their union—the evidence is in the highest degree conclusive.

I have followed, in the composition of this treatise, the same general arrangement which I adopt in my lectures. It is divided into four principal parts. The first comprehends an account of the nature and properties of *Heat, Light, and Electricity*,—agents so diffusive and subtile, that the common attributes of matter cannot be perceived in them. They are altogether destitute of weight; at least, if they possess any, it cannot be discovered by our most delicate balances, and hence they have received the appellation of *Imponderables*. They cannot be confined and exhibited in a mass like ordinary bodies; they can be collected only through the intervention of other substances. Their title to be considered material is therefore questionable, and the effects produced by them have accordingly been attributed by some to certain motions or affections of common matter. It must be admitted, however, that they appear to be subject to the same powers that act on matter in general, and that some of the laws which have been determined concerning them, are exactly such as might have been anticipated on the supposition of their materiality. It hence follows, that we need only regard them as subtile species of matter, in order that the phenomena to which they give rise may be explained in the language, and according to the principles, which are applied to material substances in general; and I shall therefore consider them as such in my subsequent remarks.

The second part comprises *Inorganic Chemistry*. It includes the doctrine of affinity, and the laws of combination, together with the chemical history of all the elementary principles hitherto discovered, and of those compound bodies which are not the product of organization. Elementary bodies are divided into the non-metallic and metallic; and the substances contained in each division are treated in the order which, it is conceived, will be most con-

venient for the purposes of teaching. From the important part which oxygen plays in the economy of nature, it is necessary to begin with the description of that principle; and from the tendency it has to unite with other bodies, as well as the importance of the compounds it forms with them, it will be useful, in studying the history of each elementary body, to describe the combinations into which it enters with oxygen gas. The remaining compounds which the non-metallic substances form with each other, will next be considered. The description of the individual metals will be accompanied by a history of their combinations, first with the simple non-metallic bodies, and afterwards with each other. The last division of this part will comprise a history of the salts.

The third general division of the work is *Organic Chemistry*, a subject which will be conveniently discussed under two heads, the one comprehending the Chemistry of the compound Radicals, the other treating of the influence of Life on Chemical Products.

The fourth part contains brief directions for the performance of *Analysis*.

ELEMENTS OF CHEMISTRY.

PART I.

IMPONDERABLE SUBSTANCES.

SECTION I.

HEAT, OR CALORIC.

THE term *Heat*, in common language, has two meanings: in the one case, it implies the sensation experienced on touching a hot body; in the other, it expresses the cause of that sensation. When used in the latter sense, it is synonymous with the word *Caloric* (from *Calor*, heat), which is employed exclusively to signify the cause or agent by which all the effects of heat are produced.

Heat, on the supposition of its being material, is a subtile fluid, the particles of which repel each other, and are attracted by all other substances. It is imponderable; that is, it is so exceedingly light, that a body undergoes no appreciable change of weight, either by the addition or abstraction of heat. It is present in all bodies, and cannot be wholly separated from them; for if a substance, however cold, be transferred into an atmosphere which is still colder, a thermometer placed in the body will indicate the escape of heat. That its particles repel one another, is proved by observing that it flies off from a heated body; and that it is attracted by other substances, is inferred from the tendency it has to penetrate their particles, and to be retained by them.

Heat may be transferred from one body to another. Thus, if a cup of mercury at 60° be plunged into hot water, heat passes rapidly from one into the other, until the temperature in both is the same; that is, till a thermometer placed in each stands at the

same height. All bodies on the earth are constantly tending to attain an equality, or what is technically called an *equilibrium*, of temperature. If, for example, a number of substances of different temperature be enclosed in an apartment, in which there is no actual source of heat, they will very soon acquire an equilibrium, so that a thermometer will stand at the same point in all. Our varying sensations of heat and cold are owing to a like cause. On touching a hot body, heat passes from it into the hand, and excites the feeling of warmth; when we touch a cold body, heat is communicated to it from the hand, and thus arises the sensation of cold.

Heat is communicated from a hot body to others which are colder in two ways, by *direct contact*, and by *radiation*. By *direct contact*, when the hot body touches a cold one, so that the heat may pass directly from one into the other; as when a bar of iron is put into a fire, or the hand plunged into hot water. By *radiation*, when the heat leaps as it were from a hot to a cold body through an appreciable interval; as when a red-hot ball, suspended in the vacuum of an air-pump, distributes its heat to surrounding objects, or when we are warmed by standing at some distance before a fire. In studying these phenomena we must regard both the loss of heat in the hot body, and the gain of heat in the cold one. The mode in which a hot body cools is, firstly, by giving off heat from its surface either by contact or radiation, or both conjointly; and secondly, by the heat in its interior passing from particle to particle through its substance to its surface. The heating of a cold body is effected, firstly, by heat passing into its surface either by contact or radiation, or by both conjointly; and, secondly, by the heat at its surface passing from particle to particle through its interior portions. Hence, in tracing the laws which regulate the distribution of heat, we shall successively consider the communication of heat from one body to another by *contact*, its passage from particle to particle of the same substance or the *conduction* of heat, and its transfer from a sensible distance or *radiation*.

COMMUNICATION OF HEAT BY CONTACT.

The principal conditions which influence the communication of heat from one body to another by contact, are the degree of contiguity, and the conducting power of the substances. The more

perfect the approximation, the more rapid, *cæteris paribus*, is the transfer. The contact of two solids, or of a solid with a gas, is in general of a less perfect kind, and at fewer points, than that between a solid and a liquid; and hence, so far as *contact alone* is concerned, the transfer is more rapid in the latter case than in the former. It is still more rapid when liquids are mixed with each other, or gases with gases, owing to the intermixture of their particles. When bodies touch each other at their surfaces only, the question becomes one of conduction, the rapidity of transfer depending on the velocity with which heat passes through the substances in contact. Thus, if a hot mass of iron and another of marble, of equal size, form, and temperature, be plunged into equal quantities of cold water, the iron will cool faster than the marble, because heat passes more rapidly through the substance of the former than through that of the latter. Were two pieces of hot iron similarly plunged, one into mercury, and the other into water, the piece in contact with mercury would cool most rapidly, because that metal is a better conductor than water. Were the experiment made by immersing the iron into mercury, and the marble into water, the rapidity of cooling in the former would very much exceed that in the latter, from two causes;—both from heat passing more rapidly through iron than through marble, and from its being conveyed away more rapidly by mercury than by water. The same principle explains the unequal sensation caused by bodies of equal temperature. Thus the hand receives a more vivid impression of warmth by touching hot iron than from glass of the same temperature; because the quantity of heat which in a given time can be brought from the interior to the surface of the hot body, so as to pass into the skin, is much greater in iron than in glass. In like manner, cold iron feels colder than glass of the same temperature, because the former conveys away from the skin more heat in a given time than the glass.

CONDUCTION OF HEAT.

By this term is expressed the passage of heat from particle to particle through the substance of bodies. Heat is said to be conducted by them or to pass by *conduction*, and the property on which its transmission depends is termed *conducting power*.

Heat obviously passes through bodies with different degrees of velocity. Some substances oppose very little impediment to its

passage, while it is transmitted slowly by others. One cannot leave one end of a rod of iron for some time in the fire, and then touch its other extremity, without danger of being burned, though this may be done with perfect safety with a rod of glass or of wood. The heat will speedily traverse the iron bar, so that at the distance of a foot from the fire it is impossible to support its heat; while we may hold a piece of red-hot glass two or three inches from its extremity, or keep a piece of burning charcoal in the hand, though the part in combustion be only a few lines removed from the skin. The observation of these and similar facts, has led to the division of bodies into *conductors* and *non-conductors* of heat. The former division, of course, includes those bodies, such as the metals, which allow heat to pass freely through their substance; and the latter comprises those which do not give an easy passage to it, such as stones, glass, wood, and charcoal.

Various methods have been adopted for determining the relative conducting power of different substances. The mode devised by Ingenhouz was to cover small rods of the same form, size, and length, but of different materials, with a layer of wax, to plunge their extremities into heated oil, and note to what distance the wax was melted on each during the same interval. The metals were found, by this method, to conduct heat better than any other substances; and of the metals, silver is the best conductor; gold comes next; then tin and copper, which are nearly equal; then platinum, iron, and lead.

Some experiments have been made by Despretz, apparently with great care, on the relative conducting power of the metals and some other substances, and the results are contained in the following table. (An. de Ch. et Ph. xxxvi. 422.)

Gold . . .	1000	Tin . . .	303.9
Silver . . .	973	Lead . . .	179.6
Copper . . .	898.2	Marble . . .	23.6
Platinum . . .	381	Porcelain . . .	12.2
Iron . . .	374.3	Fine clay . . .	11.4
Zinc . . .	363		

The substances employed for these experiments were made into prisms of the same form and size. To one extremity a constant

* Ingenhouz, Journal de Phys. 1789, p. 68.

source of heat was applied, and the passage of heat along the bar was estimated by small thermometers placed at regular distances, with their bulbs fixed in the substance of the prism.

An ingenious plan was adopted by Count Rumford (*Phil. Trans.* 1792,) for ascertaining the relative conducting power of the different materials employed for clothing. He enveloped a thermometer in a glass cylinder blown into a ball at its extremity, and filled the interstices with the substance to be examined. Having heated the apparatus to the same temperature in every instance by immersion in boiling water, he transferred it into melting ice, and observed carefully the number of seconds which elapsed during the passage of the thermometer through 185 degrees. When there was air between the thermometer and cylinder, the cooling took place in 576 seconds; when the interstices were filled with fine lint, it took place in 1032"; with cotton wool in 1046"; with sheep's wool in 1118"; with raw silk in 1284"; with beaver's fur in 1296"; with eider down in 1305"; and with hare's fur in 1315". The general practice of mankind is therefore fully justified by experiment. In winter, clothing of silk or wool is used in order to retain the animal heat; while in summer, cotton or linen stuffs are preferred, that the heat of the body may the more easily escape.

The conducting power of solid bodies does not seem to be related to any of the other properties of matter; but it approaches nearer to the ratio of their densities than to that of any other property. Count Rumford found a considerable difference in the conducting power even of the same material, according to the state in which it was employed. His observations seem to warrant the conclusion, that in the same substance the conducting power increases with the compactness of structure.

Liquids may be said, in one sense, to have the power of conveying heat with great rapidity, though in reality they are very imperfect conductors. This peculiarity is referable to the mobility which subsists among the particles of all fluids, and to the change of size which is invariably produced by a change of temperature. When any particles of a liquid are heated they expand, thereby becoming specifically lighter than those which have not received an increase of temperature; and if the former happen to be covered by a stratum of the latter, these from their greater density will descend, while the warmer and lighter particles will be pressed upwards. If, therefore, heat enter at the bottom of a vessel containing a liquid, a double set of currents must be immediately esta-

blished, the one of hot particles rising towards the surface, and the other of colder particles descending to the bottom. These currents take place with such rapidity, that if a thermometer be placed at the bottom, and another at the top of a long jar, the fire being applied below, the upper one will begin to rise almost as soon as the lower. The transport of hot particles by this process has been termed the *convection* of heat.

But if, instead of heating the bottom of the jar, the heat enter by the upper surface, very different phenomena will be observed. The intestine movements cannot then be formed, because the heated particles, from being lighter than those below them, remain constantly at the top: the heat can descend through the fluid only by transmission from particle to particle, a process which takes place so very tardily, as to have induced Count Rumford to deny that water can conduct at all. In this, however, he was mistaken; for the opposite opinion has been successfully supported by Hope, Thomson, and the late Dr. Murray, though they all admit that water, and liquids in general, mercury excepted, possess the power of conducting heat in a very slight degree.

It is extremely difficult to estimate the conducting power of æriform fluids. Their particles move so freely on each other, that the moment a particle is dilated by heat, it is pressed upwards with great velocity by the descent of colder and heavier particles, so that an ascending and descending current is instantly established. Besides, gaseous bodies allow a passage through them by radiation. Now the quantity of heat which passes by these two channels is so much greater than that which is conducted from particle to particle, that we possess no means of determining their proportion. It is certain, however, that the conducting power of gaseous fluids is exceedingly imperfect, probably even more so than that of liquids.

RADIATION.

When the hand is placed beneath a hot body suspended in the air, a distinct sensation of warmth is perceived, though from a considerable distance. This effect does not arise from the heat being conveyed by means of a hot current; since all the heated particles have an uniform tendency to rise. Neither, for reasons above assigned, can it depend upon the conducting power of the air; because aerial substances possess that power in a very low degree, while the sensation in the present case is excited almost on the

instant. There is yet another mode by which heat passes from one body to another; and as it takes place in all gases, and even *in vacuo*, it is inferred that the presence of a medium is not necessary to its passage. This mode of distribution is called *Radiation of Heat*, and the heat so distributed is called *Radiant* or *Radiated Heat*. It appears, therefore, that a heated body suspended in the air cools, or is reduced to an equilibrium with surrounding bodies, in three ways; first, by the conducting power of the air, the influence of which is very trifling; secondly, by the mobility of the air in contact with it; and thirdly, by radiation.

Laws of Distribution. Heat is emitted from the surface of a hot body equally in all directions, and in right lines, like radii drawn from the centre to the surface of a sphere; so that a thermometer placed at the same distance on any side would stand at the same point, if the effect of the ascending current of hot air could be averted. The calorific rays, thus distributed, pass freely through a vacuum and the air, without being arrested by the latter or in any way affecting its temperature. When they fall upon the surface of a solid or liquid substance they may be disposed of in three different ways:—1, they may rebound from its surface, or be *reflected*; 2, they may be received into its substance, or be *absorbed*; and, 3, they may pass directly through it, or be *transmitted*. In the first and third cases, the temperature of the body on which the rays fall is altogether unaffected; whereas, in the second, it is increased. The heating influence varies with the distance from the radiating body. The heat of a fire is less, the further we are removed from it; just as the light grows faint in proportion as we recede from a lamp. The rate or law of decrease, as ascertained by careful experiment, and as may be inferred from mathematical considerations, is, that the intensity of heat diminishes in the same ratio as the squares of the distances from the radiating point increase. Thus the thermometer will indicate four times less heat at two inches, nine times less at three inches, and sixteen times less at four inches, than it did when it was only one inch from the heated substance.

The radiation of heat by hot bodies is singularly influenced by the nature and condition of their surfaces, a circumstance which was first examined by Leslie, to whose *Essay on Heat*, published in 1804, we must still refer for most of our knowledge on this subject. Leslie employed in his experiments a hollow tin cube filled with hot water as the radiating substance. The rays proceeding

from it were brought, by means of a concave mirror, into a focus, in which the bulb of a differential thermometer was placed. By adapting thin plates of different metals to the sides of the tin cube, and turning them successively towards the mirror, he found a very variable effect produced upon the thermometer. A bright smooth polished plate of metal radiated very imperfectly; but if its surface were in the least degree dull or rough, the radiating power was immediately augmented. Or if the metallic surface were covered with a thin layer of isinglass, paper, wax, or resin, its power of radiation increased surprisingly. It follows from these researches that velocity of radiation depends more on the *surface* than the *substance* of a radiating body:—that the most imperfect radiators are to be sought among those bodies which are highly smooth and bright, such as polished gold, silver, tin, and brass; but that these same metals radiate freely when their smoothness and polish are destroyed, as by scratching their surfaces with a file, or covering them with whiting or lamp black. A metallic surface seems adverse to radiation independently of its smoothness, since a highly-polished piece of glass radiates far better than an equally polished metallic surface. Scratching a surface probably favours radiation by multiplying the number of radiating points.

Some interesting experiments have been made by Dr. Stark of Edinburgh, (Phil. Trans. 1833, Part II.) illustrative of the connexion between radiation and the colour of surfaces. The bulb of a delicate thermometer was successively surrounded by equal weights of differently coloured wool, was placed in a glass tube, heated by immersion in hot water to 180° , and then cooled to 50° in cold water. The times of cooling were 21 minutes with black wool, 26 with red wool, and 27 with white wool. Concurring results were obtained with flour of different colours. Likewise, black wool was found to collect more dew than an equal weight of white wool, other circumstances being alike.—This is the first time that direct experiments, seemingly unexceptionable, have been made in proof of the influence of colour over radiation.

Reflection of Heat.—The existence of a reflecting power may be shown by standing at the side of a fire in such a position that the heat cannot reach the face directly, and then placing a plate of tinned iron opposite the grate, and at such an inclination as permits the observer to see in it the reflection of the fire: as soon as it is brought to this inclination, a distinct impression of heat will be perceived upon the face. If a line be drawn from a radiating sub-

stance to the point of a plane surface by which its rays are reflected, and a second line from that point to the spot where its heating power is exerted, the angles which these lines form with a line perpendicular to the reflecting plane are called the angles of *incidence* and *reflection*, and are invariably equal to each other. It follows from this law, that when a heated body is placed in the focus of a concave parabolic reflector, the diverging rays which strike upon it assume a parallel direction with respect to each other; and that when these parallel rays impinge upon a second concave reflector standing opposite to the former, they are made to converge, so as to meet together in its focus. Their united influence is thus brought to bear upon a single point.

It has been known for ages that the heat contained in the solar rays admits of being reflected by mirrors, and a like property has long since been recognized in the rays emitted by red-hot bodies; but that heat emanates in invisible rays, which are subject to the same laws of reflection as those that are accompanied by light, is a modern discovery, noticed indeed by Lambert, but first decisively established by Saussure and Pictet of Geneva. They first proved it of an iron ball heated so as not to be luminous even in the dark, and then of a vessel of boiling water, (Pictet's *Essai sur le Feu*, p. 65, 1790); but for most of our knowledge of this subject we must again refer to the labours of Leslie. He demonstrated that the reflecting power depends on the nature and condition of surfaces, and that those qualities which are adverse to radiation, are precisely such as promote reflection. Bright smooth metallic surfaces, as polished silver, brass, or tin, which are retentive of their own heat, are little prone to receive heat from other sources, but cause such rays to fly off from them; while those qualities of a surface which facilitate radiation from a hot body, likewise unfit it for reflecting the rays which fall upon it from surrounding objects. His experiments, indeed, justify the conclusion that the faculty of radiation is inversely as that of reflection.

Absorption of Heat.—Every increase of temperature arising from radiant heat is due to its absorption or reception into the body on which it falls. If a pencil of heat impinge on the surface of a body, through which no portion of it is directly transmitted, it must either be absorbed or reflected: those rays which are reflected cannot be absorbed; and those which are not reflected, must be

absorbed. The number of absorbed rays is supplemental to that of the reflected rays. It hence follows that as the reflecting power is materially influenced by the nature of surfaces, the absorptive power must be so likewise. Those qualities of a surface which increase reflection are to the same extent adverse to absorption; and those which favour absorption are proportionally injurious to reflection. Since, moreover, as was shown in the last article, the property of radiation is inversely as that of reflection, the power of radiating is directly proportional to that of absorbing heat. These inferences are fully justified by the researches of Leslie, and have received additional confirmation by a decisive experiment made by my colleague, Dr. Ritchie. (Royal Inst. Journal, v. 305.)

The colour of surfaces influences the absorption of radiant heat. This has been observed by several persons of the sun's rays, and of terrestrial heat associated with light, as will be stated in the next section; but the dependance of the absorptive power for simple heat on colour has not till lately been noticed. From researches by Stark already referred to (page 16), it seems that differently coloured wools wound upon the bulb of a thermometer, and exposed within a glass tube to hot water, rose from 50° to 170° in the following times,—black wool in 4' 30", dark green in 5', scarlet in 5' 30", white in 8'.

An interesting connexion has been traced by Nobili and Melloni between the absorbing and conducting power of surfaces. (An. de Ch. et Ph. xlviii. 198.) In their experiments variations of temperature were estimated by the *thermo-multiplier*, which consists of a thermo-electric combination on the principle of those to be hereafter described in the article on *Thermo-Electricity*: it is attached to a delicate galvanometer, which, by measuring the degree of galvanic excitement, acts as a thermometer, the excitement being thought to vary directly as the temperature. These researches, if free from fallacy, justify the inference that the radiating and absorbing powers of surfaces for simple heat are in the inverse order of their conducting power.

Transmission of Heat.—Radiant heat passes with perfect freedom through a vacuum. The air and gaseous substances present but a feeble barrier to its progress; so feeble, indeed, that the degree of impediment which they occasion has not yet been appreciated. Most transparent media of a denser kind, on the contrary, such as the diamond, rock-crystal, glass, and water, even in thin

strata, interfere greatly with its passage. This last remark, however, is only applicable to *simple radiant heat*, that is, to heat unassociated with light. The solar rays pass readily through glass, both heat and light being refracted in their passage, as is shown by the action of a burning glass or lens; and though much of the heat emitted by the flame of a lamp or a red-hot ball of iron is arrested by glass, many calorific rays are directly transmitted along with the light. But the result is different when the heated body is not luminous. A thin screen of glass interposed between such an object and a thermometer certainly intercepts most of the rays that fall upon it; and the sole question which can be raised is, whether the small effect on the thermometer is caused by direct transmission, or by the screen first becoming warm by absorbing the rays, and then acting by its radiation on the thermometer. On this point the philosophic world was long much divided; but the question has been at length finally set at rest by the masterly researches of Melloni, made with the thermo-multiplier (*An. Ch. et Ph.* xlviii. 198, liii. 5, lv. 337, lx. 402). He has proved that solids and liquids differ in transmissibility to the rays of heat, just as they differ in their action on light. This may be expressed by the terms *transcalent* and *intranscalent* (*trans* through, *calco* I heat), or *diathermanous* and *adiathermanous* (*dia* through, *ἀδιαφανής* I heat), corresponding to the adjectives transparent and opaque as applied to light. The principal conclusions flowing from his researches are the following:—

1. Though transcalent bodies are also in general more or less transparent, the only known exceptions being opaque black glass and black mica, yet the transcalency and transparency of a substance are not in the same proportion. Rock-salt is far more transcalent than glass of far greater transparency. Chloride of sulphur of a reddish-brown tint is more transcalent than nut or olive oil of a light yellow colour, and these than the purest ether, alcohol, and water; while their transparency is in the opposite order.

2. Radiant heat falling perpendicularly on laminae of transcalent bodies having parallel surfaces suffers in all the same degree of reflection, which amounts to 39-1000ths of the incident rays on entering, and 37-1000th on leaving the lamina.

3. Transcalent bodies differ in the degree of their transcalency. Rock-salt is the only known substance which is perfectly diathermanous: heat from any source falling on a lamina of pure rock-salt

with parallel faces is not at all absorbed, all the rays which are not reflected being directly transmitted; and this is true whether the laminæ be thick or thin. The result is different with other translucent bodies, which always absorb a portion of the incident rays. Of 100 rays of heat from the same source successively incident on laminæ of equal thickness of rock-salt, alum, flint-glass, and crown-glass, the transmitted rays were 92, 12, 65, and 49. Of 100 rays similarly incident on strata of water, chloride of sulphur, bisulphuret of carbon, ether, and alcohol, the transmitted rays were 11, 68, 63, 21, and 15. The rays transmitted through similar laminæ of coloured glass were 53 per cent. with violet glass, 47 with red, 84 with yellow, 83 with blue, and 26 with green glass.

4. In glass and liquids those are most translucent which have the greatest refractive power in regard to light. This is shown in No. 8, where only 11 per cent. of the incident heat passed through water, and 68 through a similar stratum of bisulphuret of carbon. But the law is not applicable to crystalline bodies: thus, as above, 92 per cent. of the incident rays find their way through rock-salt, and 12 per cent. through a similar stratum of alum; while their refractive powers for light are nearly the same.

5. The quantity of radiant heat transmissible through glass varies with the temperature of the source from which the rays emanate. Of 100 rays successively incident on the same lamina of glass from the four sources, an oil-lamp, red-hot platinum, blackened copper heated to 734° , and the same copper at 212° , the number of rays transmitted were 77, 57, 84, and 12. Similar results were formerly obtained by De la Roche (Biot's *Traité de Physique*, iv. 638); and Melloni has proved that diathermanous bodies in general act in the same manner as glass. The only exception is rock-salt, which is equally permeable to rays from sources of a low as of a high temperature. It further appears that rays from the same source pass through some media more readily than through others. It seems an unavoidable inference from Melloni's experiments, that radiant heat has different properties according to its source; that there are various kinds or states of radiant heat, just as there are various kinds or states of light as manifested by its different colours. The rays of light which have passed through blue glass will pass through a second blue glass more easily than through glass of a different colour, though otherwise less opaque than the blue glass. So do calorific rays, after transmission

through water, pass through a second stratum of water more readily than through liquids otherwise more diathermanous, such as alcohol or ether. The water absorbs many rays which might have had the power to pass through alcohol, and gives passage to others which can penetrate water, but not alcohol. Hence it should follow, as Melloni has proved, that comparatively little heat is absorbed by multiplying screens of the same material, or increasing the thickness of one screen: it is the first screen, or the side of one screen, next the radiating substance, by which the principal absorption of heat is effected. The quantity of heat arrested by increasing the thickness of a screen decreases in a very rapid ratio. These facts establish between heat and light new and deeply interesting relations, which will be referred to in the next section.

6. Melloni has established the refrangibility of heat by diathermanous media. Prior observers failed of obtaining decisive evidence of this property, in consequence of using prisms or lenses of glass, the feeble transalency of which unfits it for such an inquiry; but with a prism of rock-salt Melloni easily demonstrated the general principle, and proved that heat from different sources, like light of different colours, has different degrees of refrangibility.

Polarization and double Refraction of Heat.—These properties of radiant heat, which Melloni with all his skill vainly attempted to demonstrate, have lately been established in regard to heat, both from luminous and non-luminous sources, by Forbes,—a discovery of great interest, as drawing still closer the relations of heat and light, and for which he has received the well-merited honour of the Keith medal, awarded by the Royal Society of Edinburgh. Forbes has polarized heat by all the methods which polarize light, by reflection, refraction, and double refraction. He also depolarized heat; and as this occurs only as a consequence of double refraction, he thereby proved the double refraction of heat. The instrument used by Forbes was the thermo-multiplier, brought to such extreme delicacy that it is supposed sensible to $\frac{1}{1500}$ ths of a degree of Fahrenheit's thermometer. (Phil. Trans. Ed. 1835.)

7. *Theory of Radiation.*—The tendency which all bodies give to attain an equality of temperature by means of radiation, has given rise to two ingenious theories, suggested respectively by Pictet and Prevost. According to the former, bodies of equal temperature do not radiate at all; and when the temperature is unequal, the hotter give caloric rays to the colder bodies till an equilibrium

is established, at which moment the radiation ceases. Prevost, on the contrary, conceived radiation to go on at all times, and from all substances, whether their temperature were the same or different from that of surrounding objects (*Recherches sur la Chaleur*). Consistently with this view, the temperature of a body falls whenever it radiates more heat than it absorbs; its temperature is stationary when the quantities emitted and received are equal; and it grows warm when the absorption exceeds the radiation. The first case occurs when a hot body is surrounded by others colder than itself; the second, when all the substances within the sphere of each other's radiation have the same temperature; and the third, when a body is introduced into a room which is warmer than itself. Of these theories the preference is very generally accorded to the latter. Most of the phenomena of radiation, indeed, admit of a satisfactory explanation by both; but on the whole, the theory of Prevost is more generally applicable. A favourable example for tracing this preference is afforded by the law of cooling *in vacuo*, established by Dulong and Petit. Another argument in its favour is deducible from the close analogy which subsists between the laws of heat and light. Luminous bodies certainly exchange rays with one another:—a feeble light sends rays to one of greater intensity; and the quantity of light emitted by each, does not seem to be at all influenced by the vicinity of the other. Since, therefore, the radiation of light is not prevented by the presence of other luminous bodies, it is probable that the radiation of heat is equally uninfluenced by the proximity of other radiating substances.

Adopting, for the reasons just stated, the theory of Prevost, it will be useful to examine a few instances of its application;—and, first, in regard to the experiments with conjugate mirrors. If a metallic ball in the focus of one mirror, and a thermometer in that of the other, be of the same temperature as the surrounding objects (say at 60°), the thermometer will remain stationary. It will indeed receive rays from the ball; but as it emits an equal number in return, its temperature will be unchanged. If the ball is above 60° the thermometer will rise, because it then receives a greater number of rays than it emits. If, on the contrary, the ball is below 60° , the thermometer, being the warmer of the two bodies, emits more rays than it receives, and its temperature will fall.

The same mode of reasoning explains an interesting experiment originally performed by the Florentine Academicians, and

since carefully repeated by Pictet. He placed a piece of ice instead of the metallic ball in the focus of his mirror, and observed that the thermometer in the opposite focus immediately descended, but rose again as soon as the ice was removed. On replacing the ice in the focus, the thermometer again fell, and reascended when it was withdrawn. It was supposed by some philosophers that this experiment proved the existence of frigorific rays, endowed with the property of communicating coldness; whereas, all the preceding remarks were made on the supposition that cold is merely a negative quality arising from the diminution of heat. Nor is the foregoing experiment inconsistent with such an opinion: on the contrary, it is readily accounted for by the theory of Prevost, and might have been anticipated by its application. The thermometer, in fact, has its temperature lowered, because it emits more rays than it receives; and it rises when the ice is removed, because it then receives a number of calorific rays radiated by the warmer surrounding objects, which were intercepted by the ice while it was in the focus.

An elegant application of this theory was made by Dr. Wells to account for the formation of dew. The most copious deposit of dew takes place when the weather is clear and serene; and the substances that are covered with it are always colder than the contiguous strata of air, or than those bodies on which dew is not deposited. In fact, dew is a deposition of water previously existing in the air as vapour, and which loses its gaseous form only in consequence of being chilled by contact with colder bodies. In speculating, therefore, about the cause of this phenomenon, the chief object is to discover the cause of the reduction of temperature. The explanation proposed by Wells, in his excellent Treatise on Dew, and now universally adopted, is founded on the theory of Prevost. If it be admitted that bodies radiate at all times, their temperature can remain stationary only by their receiving from surrounding objects as many rays as they emit; and should a substance be so situated that its own radiation may continue uninterruptedly without an equivalent being returned to it, its temperature must necessarily fall. Such is believed to be the condition of the ground in a calm starlight evening. The calorific rays which are then emitted by substances on the surface of the earth, are dispersed through free space and lost: nothing is present in the atmosphere to exchange rays with them, and their temperature consequently diminishes. If,

on the contrary, the weather be cloudy, the radiant heat proceeding from the earth is intercepted by the clouds, an interchange is established, and the ground retains nearly, if not quite, the same temperature as the adjacent portions of air.

All the facts hitherto observed concerning the formation of dew, tend to confirm this explanation. Dew is deposited sparingly or not at all in cloudy weather; all circumstances which promote free radiation are favourable to its deposition; good radiators of heat, such as grass, wood, the leaves of plants, and filamentous substances in general, reduce their temperature, in favourable states of the weather, to an extent of 10, 12, or even 15 degrees below that of the circumambient air; and while these are drenched with dew, pieces of polished metal, smooth stones, and other imperfect radiators, are barely moistened, and are nearly as warm as the air in their vicinity.

Cooling of Bodies.—Heated bodies cool by two very different methods (page 10). When a hot body is enveloped in solid substances, its heat is withdrawn solely by communication, and the velocity of cooling depends on the conducting power. Cooling is effected in a similar manner when the heated body is immersed in a liquid; but the velocity of cooling then depends partly on the conducting power of the liquid, and partly on the mobility of its particles. In elastic fluids the cooling takes place both by communication and radiation; and in a vacuum it is produced solely by radiation. The term *velocity of cooling* above employed signifies the number of degrees lost by a hot body during equal intervals of time, as one minute or one second; and by the *law of cooling* is meant the relation which the velocities of cooling bear to each other. The first attempt to fix the law of cooling was by Newton. Observing the velocity of cooling in a hot body to diminish continually as the excess of its temperature declined, he conceived that the heat lost during each interval of time was a constant fraction of its excess of heat at the beginning of that interval. Thus, if a body heated to 1000 degrees above the temperature of the surrounding air were to lose 1-10th of that excess, or 100 degrees, during the first second, he thought it would lose 1-10th of the remaining 900, or 90 degrees, during the next second, and 1-10th of the residual 810, or 81 degrees, during the third second; so that the number of degrees lost during the first five seconds would be 100, 90, 81, 72.9, and 65.6. These numbers would therefore denote the velocity of cool-

ing during each succeeding second ; and on examining their mutual relation, it is obvious that they constitute a geometric progression, of which 1.111 is the ratio. For $65.6 \times 1.111 = 72.9$, $65.6 \times (1.111)^2 = 80.98$, $65.6 \times (1.111)^3 = 89.96$, &c. ;—the property of a geometrical series. As this view appeared to be consistent with actual observation, Newton inferred as a general law of cooling, that while the times of cooling form an arithmetical series, the velocities of cooling are in a geometric progression.

This subject has been experimentally investigated by Dulong and Petit. (An. of Phil. xiii. 112.) They have demonstrated that Newton's law may be adopted without material error when a body is but slightly hotter than the surrounding medium, and the whole decrease of its temperature inconsiderable ; but when the range of cooling is extensive, or the original excess of heat great, the law is very defective. They have examined with consummate skill the various circumstances by which the cooling of a hot body in a vacuum, and when surrounded by an elastic fluid, is influenced ; but their inquiry is too mathematical and abstruse for the purposes of an elementary treatise.

EFFECTS OF HEAT.

The phenomena that may be ascribed to this agent, and which may therefore be enumerated as its effects, are numerous. With respect to animals, it is the cause of the feelings of cold, agreeable warmth, and burning, according to its intensity. It excites the system powerfully, and without a certain degree of it the vital actions entirely cease. Over the vegetable world its influence is obvious to every eye. By its stimulus co-operating with air and moisture, the seed bursts its envelope and yields a new plant, the buds open, the leaves expand, and the fruit arrives at maturity. With the declining temperature of the seasons the circulation of the sap ceases, and the plant remains torpid till it is again excited by the stimulus of heat.

The dimensions of every kind of matter are regulated by this principle. Its increase, with few exceptions, separates the particles of bodies to a greater distance from each other, producing expansion, so that the same quantity of matter is thus made to occupy a larger space ; and the diminution of heat has an opposite effect. Were the repulsion occasioned by this agent to cease entirely, the atoms of bodies would come into actual contact.

The form of bodies is dependent on heat. By its increase solids are converted into liquids, and liquids are dissipated in vapour; by its decrease vapours are condensed into liquids, and these become solid. If matter ceased to be under the influence of heat, all liquids, vapours, and doubtless even gases, would become permanently solid; and all motion on the surface of the earth would be arrested.

When heat is accumulated to a certain extent in bodies, they shine or become *incandescent*. On this important property depend all our methods of artificial illumination.

Heat exerts a powerful influence over chemical phenomena. There is, indeed, scarcely any chemical action which is not in some degree modified by this principle; and hence a knowledge of its laws is indispensable to the chemist. By its means bodies previously separate are made to combine, and the elements of compounds are disunited. An undue proportion of it is destructive to all organic and many mineral compounds; and it is essentially concerned in combustion, a process so necessary to the wants and comforts of man.

Of the various effects of heat above enumerated, several will be discussed in other parts of the work. In this place it is proposed to treat only of its influence over the dimensions and form of bodies, a subject which will be conveniently studied under the three heads of expansion, liquefaction, and vaporization.

EXPANSION.

One of the most remarkable properties of heat is the repulsion which exists among its particles, a property which enables it, on entering into a body, to remove the integrant molecules of the substance to a greater distance from each other. The body, therefore, becomes less compact than before, occupies a greater space, or, in other words, expands. This effect of heat is opposed to cohesion—that force which tends to make the particles of matter approximate, and which must be overcome before any expansion can ensue. A small addition of heat should therefore occasion a small expansion, and a greater addition of heat a greater expansion; because in the latter case, the cohesion will be more overcome than in the former. Also, whenever heat passes out of a body, the cohesion being more feebly opposed, a contraction should ensue; so that expansion is only a transient effect, occasioned

solely by the accumulation of heat. Heat, moreover, should produce the greatest expansion in those bodies which are least influenced by cohesion, an inference fully justified by observation. Thus the force of cohesion is greatest in solids, less in liquids, and least of all in æriform substances; while the expansion of solids is trifling, that of liquids much more considerable, and that of elastic fluids far greater.

It may be laid down as a rule, the reason of which will now be obvious, that all bodies are expanded by heat, and that the expansion of the same body increases with the quantity of heat which enters it. But this law does not apply, unless the form and chemical constitution of the body is preserved. For if a change in either be occasioned, then the reverse of expansion may ensue; not, however, as the direct consequence of an augmented temperature, but as the result of a change in form or composition.

To prove the expansion of solids, we need only take the exact dimensions in length, breadth, and thickness, of any substance when cold, and measure it again while strongly heated, when it will be found to have increased in every direction. A familiar demonstration of the fact may be afforded by adapting a ring to an iron rod, the former being just large enough to permit the latter to pass through it while cold. The rod is next heated, and will then no longer pass through the ring. This dilatation from heat and consequent contraction in cooling take place with a force which appears to be irresistible.

The expansion of solids has engaged the attention of several experimenters, who have endeavoured to determine the exact quantity by which different substances are lengthened by a given increase of heat, and whether or not their elongation is equable at different temperatures. The Philosophical Transactions contain various dissertations on the subject by Ellicot, Smeaton, Troughton, and Roy; and Biot has given the results of experiments performed with great care by Lavoisier and Laplace, who have established the following points:—1. Different solids do not expand to the same degree from equal additions of heat. 2. A body which has been heated from the temperature of freezing to that of boiling water, and again allowed to cool to 32° , recovers precisely the same volume which it possessed at first. 3. The dilatation of the more permanent or infusible solids is very uniform within certain limits; their expansion, for example, from the freezing point of water to

122°, is equal to what takes place between 122° and 212°. The subsequent researches of Dulong and Petit (Ann. de C. et P. viii) prove that solids do not dilate uniformly at high temperatures, but expand in an increasing ratio; that is, the higher the temperature beyond 212°, the greater the expansion for equal additions of heat. It is manifest, indeed, from their experiments, that the rate of expansion is an increasing one even between 32 and 212°; but the differences which exist within this small range are so inconsiderable as to escape observation, and for most practical purposes may be disregarded.

The subjoined table includes the most interesting results of Lavoisier and Laplace. (Biot, i. 158.)

Names of Substances.	Elongation when heated from 32 to 212°.
Glass tube without lead, a mean of three specimens	$\frac{1}{112}$ of its length.
English flint glass	$\frac{1}{127}$
Copper	$\frac{1}{100}$
Brass—mean of two specimens	$\frac{1}{83}$
Soft iron forged	$\frac{1}{110}$
Iron wire	$\frac{1}{112}$
Untempered steel	$\frac{1}{117}$
Tempered steel	$\frac{1}{107}$
Lead	$\frac{1}{47}$
Tin of India	$\frac{1}{18}$
Tin of Falmouth	$\frac{1}{28}$
Silver	$\frac{1}{34}$
Gold—mean of three specimens	$\frac{1}{50}$
Platinum, determined by Borda	$\frac{1}{100}$

Knowing the elongation of any substance for a given number of degrees of the thermometer, its total increase in bulk may in general be calculated by trebling the number which expresses its increase in length. Thus if a tube of flint glass elongates by $\frac{1}{127}$, when heated from the freezing to the boiling point of water, its cubic space will have increased by $\frac{3}{127}$ or $\frac{1}{42}$ of its former capacity. Strictly speaking this rule is not exact; but when the expansion of any substance, corresponding to the observed increase of temperature, is a minute fraction of its volume, the formula may be applied with safety. The error is then so small that it may be disregarded.

The reason of this is easily explained on geometric principles. Let l be the length of a cold metallic bar, and v its volume or solidity; let $l+d$ be its length when heated, and $v+d^3$ its volume in that state. As its breadth and thickness increase in the same proportion as its length, the expanded bar will have precisely the same figure, that is, the same proportion of its dimensions, as the cold one; and since, by Euclid, the solidity of similar figures is as the cube of homologous sides, it follows that $v : v+d^3 :: l^3 : (l+d)^3$ or $1 : 1+\frac{d}{l} + 3\frac{d^2}{l^2} + \frac{d^3}{l^3}$. When, in solids, liquids, or gases, d happens to be a very small fraction, d^2 and even d^3 are extremely minute, and may hence be altogether neglected.

The expansion of glass, iron, copper, and platinum, has been particularly investigated by Dulong and Petit. The following table contains the result of their observations on glass. (Ann. de Ch. et Ph. vii. 138.) It appears from the third column that at temperatures beyond 212° glass expands in a greater ratio than mercury.

Temperature by an air thermometer.	Mean absolute dilatation of glass for each degree.	Temperature by a thermometer made of glass.
Fahr.	Fahr.	Fahr.
From 32° to 212°	$\frac{1}{100000}$	212
— 32 to 392	$\frac{1}{99999}$	415.8
— 32 to 572	$\frac{1}{99998}$	667.2

The second, fourth, and sixth columns of the following table show the mean total expansion of iron, copper, and platinum, when heated from 32° to 212° and from 32 to 572° , for each degree. The third, fifth, and seventh columns indicate the degrees on a thermometer of iron, copper, and platinum, corresponding to a temperature of 572° on an air thermometer. It is obvious that platinum is much more uniform in its expansion than either of the other metals.

Temp. by air thermometer.	Mean dilat. of iron in volume for each degree.	Temp. by iron rod thermometer.	Mean dilat. of copper in volume for each degree.	Temp. by copper rod thermometer.	Mean dilat. of platinum in volume for each degree.	Temp. by platinum rod thermometer.
Fahr.	Fahr.	Fahr.	Fahr.	Fahr.	Fahr.	Fahr.
212°	$\frac{1}{100000}$	212°	$\frac{1}{100000}$	212°	$\frac{1}{100000}$	212°
572°	$\frac{1}{99999}$	702.5	$\frac{1}{99999}$	623.8	$\frac{1}{99998}$	592.9

The expansion of liquids is proved by putting a common thermometer, made with mercury or alcohol, into warm water, when the dilatation of the liquid will be shown by its ascent in the stem. The experiment is indeed illustrative of two other facts. It proves, first, that the dilatation increases with the temperature; for if the thermometer be plunged into several portions of water heated to different degrees, the ascent will be greatest in the hottest water, and least in the coolest portions. It demonstrates, secondly, that liquids expand more than solids. The glass bulb of the thermometer is itself expanded by the hot water, and therefore is enabled to contain more mercury than before; but the mercury being

dilated to a much greater extent, not only occupies the additional space in the bulb, but likewise rises in the stem. Its ascent marks the difference between its own dilatation and that of the glass, and is only the apparent, not the actual, expansion of the liquid.

Different liquids do not expand to the same degree from an equal increase of temperature. Alcohol expands much more than water, and water than mercury. From the frequency with which the latter is employed in philosophical experiments, it is important to know the exact amount of its expansion. This subject has been investigated by several philosophers, but the experiments of Lavoisier and Laplace, and especially of Dulong and Petit, from the extreme care with which they were made, are entitled to the greatest confidence. According to the former the actual dilatation of mercury, in passing from the freezing to the boiling point of water, amounts to $\frac{1.00}{544\frac{1}{2}}$ of its volume; but the result obtained by Dulong and Petit, who found it $\frac{1.00}{555.6}$, is probably still nearer the truth. Adopting the last estimate, this metal dilates, for every degree of Fahrenheit's thermometer, $\frac{1}{999.0}$ of the bulk which it occupied at the temperature of 32° . If the barometer, for instance, stand at 30 inches when the thermometer is at 32° , we may calculate what its elevation ought to be when the latter is at 60° , or at any other temperature.* The apparent expansion of mercury contained in

* The pressure exerted by equal columns of a fluid, or fluids, is as the density of the columns; and as the density of mercury diminishes with increase of temperature, it follows that a 30-inch column of mercury at 32° has a greater weight, or presses more, than a mercurial column of equal base and height at 60° . It is hence necessary, in estimating atmospheric pressure by the barometer, either to have the mercurial column always at the same temperature, or to correct the error arising from difference of temperature by calculation. This correction is effected by finding the length or height of a mercurial column at some standard temperature, as at 60° , which shall exert the same pressure as another column at any other temperature. The formula is thus deduced:—Let H, D, V , be the height, density, and volume of a mercurial column at 32° ; and H', D', V' , its height, density, and volume when the temperature rises above 32° by any number of degrees expressed by T' . Now it is a principle in hydrostatics that the heights of fluid columns of equal pressure are inversely as their density, so that $\frac{H}{H'} = \frac{D'}{D}$,

and since the volume of the same liquid is also inversely as its density, $\frac{V}{V'} = \frac{D'}{D}$. Conse-

quently, the heights are directly as the volumes, or $\frac{H}{H'} = \frac{V}{V'}$. Since, therefore, $V' = V + V \times \frac{T'}{9990}$, so is $H' = H + H' \times \frac{T'}{9990} = H \times \left(1 + \frac{T'}{9990}\right) = H \times \left(\frac{9990 + T'}{9990}\right)$. The

glass is of course less than the absolute expansion. Between the limits of 32° and 212° Lavoisier and Laplace estimate the apparent expansion at $\frac{1}{27}$, and Dulong and Petit at $\frac{1}{27.5}$ of its volume, being $\frac{1}{11.634}$ for each degree of Fahrenheit's thermometer. Dulong and Petit state that the mean total expansion of mercury from 32° to 572° for each degree is $\frac{1}{63.46}$; and that the mean apparent expansion in glass from 32° to 572° for each degree is $\frac{1}{11.372}$. The temperature in their experiments was estimated by an air thermometer, which they consider more uniform in its rate of expansion than one of mercury. The temperature of 572° on the air thermometer corresponds to 586° in the mercurial one.

All experimenters agree that liquids expand in an increasing ratio, or that equal increments of heat cause a greater dilatation at high than at low temperatures. Thus, if a fluid is heated from 32° to 122° it will not expand so much as it would do in being heated from 122° to 212° , though an equal number of degrees is added in both cases. In mercury the first expansion, according to Deluc, is to the second as 14 to 15; in olive oil as 13.4 to 15; in alcohol as 10.9 to 15; and in pure water as 4.7 to 15. Attempts have been made to discover a law by which this progression is regulated, and Dalton conceives that the expansion observes the ratio of the square of the temperature estimated from the point of congelation, or of greatest density; but this opinion is merely hypothetical, and has been shown by Dulong and Petit to be inconsistent with the facts established by their experiments.

There is a peculiarity in the effect of heat upon the bulk of some fluids; namely, that at a certain temperature increase of heat causes them to contract, and its diminution makes them expand. This singular exception to the general effect of heat is only observable in those liquids which increase in bulk in passing from the liquid to the solid state, and is remarked only within a few degrees

value of H is, of course, found by the formula $H = H' \times \left(\frac{9990}{9990 + T'} \right)$. If, in the formula for H' , we substitute for H and T' their value as stated in the text, we shall find $H' = 30 \times \left(\frac{9990 + 28}{9990} \right) = 30.084$, which is the length of a mercurial column at 60° ,

having the same pressure as a column of mercury at 32° .

The rate of the *actual* and not *apparent* expansion is used in these formulæ, because the length of the mercurial column, depending on atmospheric pressure, is not affected by the expansion or contraction of the tube.

of temperature above their point of congelation. Water is a noted example of it. Ice swims upon the surface of water, and therefore must be lighter than it, a convincing proof that water in the act of freezing must expand. The specific gravity of ice is nearly 0.92, which gives the volume of ice to that of water as 1 to 0.92; that is, water expands by about 1-11th of its volume in passing into ice.

The most remarkable circumstance attending this expansion, is the great force with which it is effected. Boyle filled a brass tube, three inches in diameter, with water, and confined it by means of a moveable plug; the expansion, when it froze, took place with such violence as to push out the plug, though preserved in its situation by a weight equal to 74 pounds. The Florentine Academicians burst a hollow brass globe, whose cavity was only an inch in diameter, by freezing the water with which it was filled; and it has been estimated that the expansive power necessary to produce such an effect was equal to a pressure of 27,720 pounds weight. Major Williams gave ample confirmation of the same fact by some experiments which he performed at Quebec in the years 1784 and 1785. (Phil. Trans. Ed. ii. 23.)

But it is not only during the act of congelation that water expands; since it begins to dilate some time before it actually freezes. Dr. Croune noticed this phenomenon so early as the year 1683, and it has since been observed by various philosophers. To render this obvious, fill a flask, capable of holding three or four ounces, with water at the temperature of 60°, and adapt to it a cork, through which passes a glass tube open at both ends, about the eighth of an inch wide, and ten inches long. After having filled the flask, insert the cork and tube, and pour a little water into the latter till the liquid rises to the middle of it. On immersing the flask into a mixture of pounded ice and salt, the water at first contracts, and therefore descends in the tube; but soon after an opposite movement ensues, indicating dilatation, though the water within the flask is at the same time yielding heat to the freezing mixture in which it is immersed.

To the inference deduced from this experiment it was objected, that the ascent of the water in the tube is not referable to expansion in the liquid, but to contraction of the flask, diminishing its capacity. In fact, this cause does operate, though not to a degree sufficient to account for the whole effect; and, accordingly, it has been proved by an elegant and decisive experiment of Dr. Hope,

that water does really expand previous to congelation. He believes the greatest density of water to be between $39^{\circ}5'$ 40° ; that is, boiling water obeys the usual law till it has cooled to the temperature of about 40° , after which the abstraction of heat produces increase instead of decrease of volume (Phil. Trans. Ed. v. 379). Hallström, who has examined this point with much care, estimates it at 39° .

The cause of the expansion of water at the moment of freezing is attributed to a new and peculiar arrangement of its particles. Ice is in reality crystallized water, and during its formation the particles arrange themselves in ranks and lines, which cross each other at angles of 60° and 120° , and consequently occupy more space than when liquid. This may be seen by examining the surface of water while freezing in a saucer. No very satisfactory reason has been assigned for its expansion prior to congelation. It is supposed, indeed, that the water begins to arrange itself in the order it will assume in the solid state before actually laying aside the liquid form; and this explanation is generally admitted, not so much because it has been proved to be true, but because no better has been offered.

Water is not the only liquid which expands under reduction of temperature, as the same effect has been observed in a few others which assume a highly crystalline structure on becoming solid;—fused iron, antimony, zinc, and bismuth, are examples of it. Mercury is a remarkable instance of the reverse; for when it freezes, it suffers a very great contraction.

As the particles of air and æriform substances are not held together by cohesion, it follows that increase of temperature must occasion a considerable dilatation of them; and, accordingly, they are found to dilate from equal additions of heat much more than solids or liquids. Now, chemists are in the habit of estimating the quantity of the gases employed in their experiments by measuring them; and since the volume occupied by any gas is so much influenced by temperature, it is essential to accuracy that a due correction be made for the variations arising from this cause; that they should know how much dilatation is produced by each degree of the thermometer, whether the rate of expansion is uniform at all temperatures, and whether that ratio is the same in all gases.

This subject had been unsuccessfully investigated by several

philosophers, who failed in their object chiefly because they neglected the precaution of drying the gases upon which they operated; but at last the law of dilatation was detected by Dalton and Gay-Lussac nearly at the same time. Dalton's method of operating (*Manchester Memoirs*, v.) was exceedingly simple. He filled with dry mercury a graduated tube, closed at one end and carefully dried; and then, plunging the open end of the tube into a mercurial trough, introduced a portion of dry air. After having marked the bulk and temperature of the air, he exposed it to a gradually increasing heat, the exact amount of which was regulated by a thermometer, and observed the dilatation occasioned by each increase of temperature. The apparatus of Gay-Lussac (*An. de Ch.* v. 43) was the same in principle, but more complicated, in consequence of the precautions he took to avoid every possible source of fallacy.

It is proved by the researches of these philosophers, that all gases undergo equal expansions by the same addition of heat, supposing them placed under the same circumstances; so that it is sufficient to ascertain the law of expansion observed by any one gas, in order to know the law for all. The experiments of Gay-Lussac shew, that 100 parts of air in being heated from 32° to 212° expand to 137.5 parts. The increase for 180 degrees is therefore 0.375 or $\frac{3}{8}$ ths of its bulk; and by dividing this number by 180, it is found that a given quantity of dry air dilates to $\frac{1}{480}$ th of the volume it occupied at 32° , for every degree of Fahrenheit's thermometer. The result of Dalton's experiments corresponds very nearly with the foregoing.

This point being established, it is easy to ascertain what volume any given quantity of gas should occupy at any given temperature. Suppose a certain portion of gas to occupy 20 measures of a graduated tube at 32° , it may be desirable to determine what would be its bulk at 42° . For every degree of heat it has increased by $\frac{1}{480}$ th of its original volume, and therefore, since the increase amounts to ten degrees, the 20 measures will have dilated by $\frac{10}{480}$ ths. The expression will therefore be $20 + 20 \times \frac{10}{480} = 20.416$. The volume which the gas occupies at 32° is a necessary element in all such calculations. Thus, having 20.416 measures of gas at 42° , the corresponding bulk for 52° cannot be calculated by the formula $20.416 + 20.416 \frac{10}{480}$; the real expression is $20.416 + 20 \frac{10}{480}$, because the increase is only $\frac{10}{480}$ ths of the space occupied at 32° , which is 20

measures.* A similar remark applies to the formula for estimating the effect of heat on the height of the barometer.

The rate of expansion of atmospheric air at temperatures exceeding 212° has been examined by Dulong and Petit, and the following table contains the result of their observations. (An. de Ch. et Ph. vii. 120.)

Temperature by the Mercurial Thermometer.		Corresponding volumes of a given volume of air.
Fahrenheit.	Centigrade.	
— 33	— 36..	0.8650
32	0..	1.0000
212	100..	1.3750
302	150..	1.5576
392	200..	1.7389
482	250..	1.9189
572	300..	2.0976
M. boils 680	360..	2.3125

Hydrogen gas was found to expand in the same proportion, so that all gases may be inferred to expand to the same extent, for

* The following are convenient general formulæ for these calculations:—Let P' be the volume of gas at any temperature above 32°, T' the number of degrees above that point, and P its volume at 32°. Then $P' = P \times \left(1 + \frac{T'}{480}\right) = P \times \left(\frac{480 + T'}{480}\right)$; and if P is unknown, its value, deduced from the last equation, may be calculated from the formula $P = P' \times \left(\frac{480}{480 + T'}\right)$.

It frequently happens, in the employment of Fahrenheit's thermometer, that when P' for the above formula is known, it is not P itself which is wanted, but the volume of gas at some other temperature, as at 60° F. This value may be obtained without first calculating what P is. Thus, retaining the value of P' and T' as in the preceding formula, let P'' be the corresponding quantity of gas at some other temperature, the degrees of which above 32° may be expressed by T'' . Now $P'' = \frac{(480 + T'')}{480} \times P$; but as P is unknown, let its value in P' be substituted. Thus, $P'' = \left(\frac{480 + T''}{480}\right) \times \left(\frac{P' 480}{480 + T'}\right)$; which gives $P'' = \frac{480^2 P' + 480 T'' P'}{480^2 + 480 T'} = \frac{P' 480 (480 + T'')}{480 (480 + T')} = \frac{P' (480 + T'')}{480 + T'}$.

Suppose, for example, a portion of gas occupies 100 divisions of a graduated tube at 48°, how many will it fill at 60° F.? Here $P' = 100$; $T' = 48 - 32$ or 16; $T'' = 60 - 32$, or 28. The number sought, or the $P'' = \frac{100 \times 508}{496} = 102.42$.

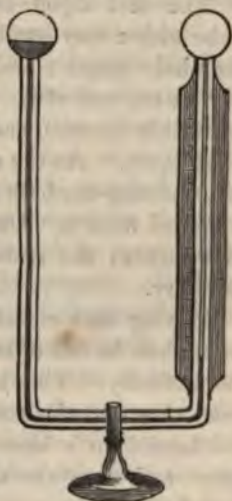
equal increments of heat, between -33° and 680° ; and the same law probably prevails at all temperatures.

ON THE THERMOMETER.

The influence of heat over the bulk of bodies is better fitted for estimating a change in the quantity of that agent than any other of its properties; for substances not only expand more and more as the temperature increases, but in general return exactly to their original volume when the heat is withdrawn. The first attempt to measure the intensity of heat on this principle was made early in the seventeenth century, and the honour of the invention is by some bestowed on Sanctorius, by others on Cornelius Drebel, and by others on the celebrated Galileo. The material used by Sanctorius was atmospheric air. The construction of the thermometer itself, or *thermoscope* as it was sometimes called, is exceedingly simple. A glass tube is to be selected for the purpose, and one end of it is blown out into a spherical cavity, while its other extremity is left open. After expelling a small quantity of air by heating the ball gently, the open end of the tube is plunged into coloured water, and a portion of the liquid is forced up into the tube by the pressure of the atmosphere, as the air within the ball contracts. In this state it indicates changes of temperature with extreme delicacy, the alternate expansion and contraction of the confined air being rendered visible by the corresponding descent and ascent of the coloured water in the stem. The material used in its construction, also, is peculiarly appropriate, because air, like all gases, expands uniformly by equal increments of heat. There are, however, two forcible objections to the general employment of this thermometer. In the first place, its dilatations and contractions are so great, that it is inconvenient to measure them when the change of temperature is considerable; and, secondly, its movements are influenced by pressure, as well as by heat, so that the instrument would be affected by variations of the barometer, though the temperature should be quite stationary.

For the reasons just stated, the common air thermometer is rarely employed; but a modification of it, described in 1804 by Leslie in his *Essay on Heat* under the name of *Differential Thermometer*, is entirely free from the last objection, and is admirably fitted for some special purposes. This instrument was invented a

century and a half ago by Sturm, Professor of Mathematics at Altdorff, who has left a description and sketch of it in his *Collegium Curiosum*, p. 54, published in the year 1676; but like other air thermometers it had fallen into disuse, till it was again brought into notice by Leslie. As now made it consists of two thin glass balls joined together by a tube, bent twice at a right angle, as represented in the annexed figure. Both balls contain air, but the greater part of the tube is filled with sulphuric acid coloured with carmine. It is obvious that this instrument cannot be affected by any change of temperature acting equally on both balls; for as long as the air within them expands or contracts to the same extent, the pressure on the opposite surfaces of the liquid, and consequently its position, will continue unchanged. Hence the differential thermometer stands at the same point, however different may be the temperature of the medium. But the slightest difference between the temperature of the two balls will instantly be detected; for the elasticity of the air on one side being then greater than that on the other, the liquid will retreat towards the ball whose temperature is lowest.



Solid substances are not better suited to the construction of a thermometer than gases; for while the expansion of the latter is too great, that of the former is so small that it cannot be measured except by the adaptation of complicated machinery. Liquids which expand more than the one and less than the other, are exempt from both extremes; and, consequently, we must search among them for a material with which to construct a thermometer. The principle of selection is plain. A material is required whose expansions are uniform, and whose boiling and freezing points are very remote from one another. Mercury fulfils these conditions better than any other liquid. No fluid can support a greater degree of heat without boiling than mercury; and none, except alcohol and ether, can endure a more intense cold without freezing. It has, besides, the additional advantage of being more sensible to the action of heat than other liquids, while its dilatations between

32° and 212° are almost perfectly uniform. Strictly speaking, the same quantity of heat does occasion a greater dilatation at high than at low temperatures, so that, like other fluids, it expands in an increasing ratio. But it is remarkable that this ratio, within the limits assigned, is exactly the same as that of glass; and therefore, if contained in a glass tube, the increasing expansion of the vessel compensates for that of the mercury.

The first object in constructing a thermometer is to select a tube with a very small bore, which is of the same diameter through its whole length; and then, by melting the glass, to blow a small ball at one end of it. The mercury is introduced by rarefying the air within the ball, and then dipping the open end of the tube into that liquid. As the air cools and contracts, the mercury is forced up, entering the bulb to supply the place of the air which had been expelled from it. Only a part of the air, however, is removed by this means; the remainder is driven out by the ebullition of the mercury.

Having thus contrived that the bulb and about one-third of the tube shall be full of mercury, the next step is to seal the open end hermetically. This is done by heating the bulb till the mercury rises very near the summit, and then suddenly darting a fine-pointed flame from a blow-pipe across the opening, so as to fuse the glass and close the aperture before the mercury has had time to recede from it.

The construction of a thermometer is now so far complete that it affords a means of ascertaining the comparative temperature of bodies; but it is deficient in one essential point, namely, the observations made with different instruments cannot be compared together. To effect this object, the thermometer must be graduated; a process which consists of two parts. The first and most important is to obtain two fixed points which shall be the same in every thermometer. The practice now generally followed for this purpose was introduced by Newton, and is founded on the fact, that when a thermometer is plunged into ice that is dissolving, and into water which is boiling, it constantly stands at the same elevations in all countries, provided there is a certain conformity of circumstances. The point of congelation is easily determined. The instrument is to be immersed in snow or pounded ice, which is liquefying in a moderately warm atmosphere, till the mercury becomes stationary. To fix the boiling point is a more delicate ope-

ration, since the temperature at which water boils is affected by various circumstances which will be more particularly mentioned hereafter. It is sufficient to state the general directions at present;—that the water be perfectly pure, free from any foreign particles, and not above an inch in depth,—the ebullition brisk, and conducted in a deep metallic vessel, so that the stem of the thermometer may be surrounded by an atmosphere of steam, and thus exposed to the same temperature as the bulb,—the vapour be allowed to escape freely,—and the barometer stand at 30 inches.

The second part of the process of graduation consists in dividing the interval between the freezing and boiling points of water into any number of equal parts or degrees, which may be either marked on the tube itself, by means of a diamond, or first drawn upon a piece of paper, ivory, or metal, and afterwards attached to the thermometer. The exact number of degrees into which the space is divided, is not very material, though it would be more convenient did all thermometers correspond in this respect. Unfortunately this is not the case. In Britain we use Fahrenheit's scale; the Continental philosophers employ either the centigrade, or that of Reaumur. The centigrade is the most convenient in practice; its boiling point is 100, that of melting snow is the zero, or beginning of the scale, and the interval is divided into 100 equal parts. The interval in the scale of Reaumur is divided into 80 parts, and in that of Fahrenheit into 180; but the zero of Fahrenheit is placed 32 degrees below the temperature of melting snow, and on this account the point of ebullition is 212°.

It is easy to reduce the temperature expressed by one thermometer to that of another, by knowing the relation which exists between their degrees. Thus, 180 is to 100 as 9 to 5, and to 80 as 9 to 4; so that nine degrees of Fahrenheit are equal to five of the centigrade, and four of Reaumur's thermometer. Fahrenheit's is therefore reduced to the centigrade scale, by multiplying by five, and dividing by nine; or to that of Reaumur, by multiplying by four instead of five. Either of these may be reduced to Fahrenheit by reversing the process; the multiplier is nine in both cases, and the divisor four in the one and five in the other. But it must be remembered in these reductions, that the zero of Fahrenheit's thermometer is 32 degrees lower than that of the centigrade or Reaumur, and a due allowance must be made for this circumstance. An example will best show how this is done. To reduce 212° to

the centigrade, first subtract 32, which leaves 180; and this number multiplied by $\frac{5}{9}$, gives the corresponding expression in the centigrade scale. Or to reduce 100° C. to Fahrenheit, multiply by $\frac{9}{5}$, and then add 32. To save the trouble of such reductions, I have subjoined a table, which shows the degrees on the centigrade scale and that of Reaumur, corresponding to the degrees of Fahrenheit's thermometer.

Fahr.	Cent.	Reaum.	Fahr.	Cent.	Reaum.	Fahr.	Cent.	Reaum.
212	100	80	113	45	36	14	-10	- 8
203	95	76	104	40	32	5	-15	-12
194	90	72	95	35	28	4	-20	-16
185	85	68	86	30	24	-13	-25	-20
176	80	64	77	25	20	-22	-30	-24
167	75	60	68	20	16	-31	-35	-28
158	70	56	59	15	12	-40	-40	-32
149	65	52	50	10	8			
140	60	48	41	5	4			
131	55	44	32	0	0			
122	50	40	23	-5	-4			

The mercurial thermometer may be made to indicate temperatures which exceed 212°, or fall below zero, by continuing the degrees above and below those points. But as mercury freezes at 39 degrees below zero, it cannot indicate temperatures below that point; and indeed the only liquid which has been used for such purposes is alcohol. Our means of estimating high degrees of heat are as yet very unsatisfactory. Mercury is preferable to any other liquid; but even its indications cannot be altogether relied on. For, in the first place, its expansion for equal increments of heat is greater at high than at low temperatures; and, secondly, glass expands at temperatures beyond 212° in a more rapid ratio than mercury, and consequently, from the proportionally greater capacity of the bulb, the apparent expansion of the metal is considerably less than its actual dilatation. Thus Dulong and Petit observed, that when the air thermometer is at 572°, the common mercurial thermometer stands at 586°; but when corrected for the error caused by the glass, it indicates a temperature of 597.5°. No liquid can be employed for temperatures which exceed 662°, since all of them are then either dissipated in vapour, or decomposed. Mr. Bellain has observed that mercurial thermometers slowly change their point of zero, which uniformly becomes higher than at the time of graduation. This phenomenon appears owing to a di-

minished capacity of the bulb due to the atmosphere continually pressing on its exterior, while a vacuum exists in the interior of the tube; for it has not been noticed either in mercurial thermometers which are unsealed, or in thermometers made with alcohol. The principal contraction ensues soon after the tube is sealed, and hence some months should be permitted to elapse between the sealing and graduation of a thermometer. (An. de Ch. et Ph. xxi. 330.)

The instruments for measuring intense degrees of heat are called *pyrometers*, and must be formed either of solid or gaseous substances. The former alone have been hitherto employed, though the latter, from the greater uniformity with which they expand, are better calculated for the purpose. The action of most pyrometers depends on the elongation of a metallic bar by heat; and the difficulty in their construction consists in finding an infusible metal of uniform expansibility, and in measuring the degree of expansion with exactness. The best of these is Daniell's pyrometer, which, with a little practice, may be used with facility, and appears susceptible of very great precision. (Phil. Trans. 1830 and 31.) This instrument consists of two parts, the *Register* and *Scale*, the former designed for exposure to the heat to be estimated, and the latter for measuring the exact amount of expansion. The first consists of a bar of black lead earthenware, in which is drilled a hole $\frac{3}{10}$ ths of an inch in diameter, and $7\frac{1}{2}$ inches deep. Into this hole a cylindrical bar of platinum or soft iron, of nearly the same diameter, and $6\frac{1}{2}$ inches long, is introduced, so as to rest against the solid end of the hole; and upon the outer or free end of the metallic bar rests a cylindrical piece of porcelain, called the index, $1\frac{1}{2}$ inch long, and is kept firmly in its place by a strap of platinum and a little wedge of earthenware. The object of this arrangement is, that when the register is heated, the metal expanding at each temperature more than the earthenware case, presses forward the index; and as this last moves with friction in consequence of the strap and wedge, it remains in its place when the register is removed from the fire and cooled. The scale is an instrument designed for measuring with minute accuracy the precise extent to which the index has been pushed forward by the metallic bar. It thus indicates the apparent elongation of the bar, that is, the difference between its elongation and that of the black lead case which contains it. For its indications to be correct, that is, in order that equal dilatations should indicate equal increments of heat, it is ne-

cessary that the bar and its case should both expand uniformly, or both vary at the same rate. Now in regard to the black lead case, its total expansion is so very small, that any want of uniformity at intermediate points cannot be detected; but since, as will shortly be more fully stated, all earthenware and other argillaceous substances contract when first heated, the case must not be used in pyrometry until it has been exposed in close vessels to at least as high a temperature as that which will afterwards be employed. As for the expansions of the metallic bar, these are not exactly uniform; but still they afford a good practical index of the relative intensity of different fires, and will be an exact measure of temperature when the precise rate of expansion shall have been determined.

The pyrometer of Wedgewood acts on a different principle, being founded on the property which clay, a compound of aluminous earth and water, possesses of gradually losing its water when exposed to an increasing temperature, and of contracting as the water is dissipated. The contraction even continues after every trace of water has been removed, owing to partial vitrification occurring, which tends to bring the particles of the clay into still nearer proximity. The intensity of the heat may therefore in some measure be estimated by the degree of contraction which it has occasioned.

The apparatus consists of a metallic groove, 24 inches long, the sides of which converge, being half an inch wide above, and three-tenths below. The clay, well washed, is made up into little cylinders or truncated cones which fit the commencement of the groove, after having been heated to redness; and their subsequent contraction by heat is determined by allowing them to slide from the top of the groove downwards, till they arrive at a part of it through which they cannot pass. Wedgewood divided the whole length of the groove into 240 degrees, each of which he supposed equal to 180 of Fahrenheit; and he fixed the zero of his scale at the 1077th degree of Fahrenheit's thermometer.

Wedgewood's pyrometer is no longer employed by scientific men, because its indications cannot be relied on. Every observation requires a separate piece of clay, and the observer is never sure that the contraction of the second piece, from the same heat, will be exactly similar to that of the first; especially as it is difficult to procure specimens of the earth, the composition of which is in

every respect the same. It is doubtful, too, if its point of zero has been correctly estimated; and Guyton de Morveau has shown that each degree corresponds rather to 62.5 than to 180 degrees of Fahrenheit.

For some purposes, especially in making meteorological observations, it is desirable to ascertain the highest and lowest temperature which has occurred in a given interval of time, during the absence of the observer. The instruments employed with this intention are *Register Thermometers*, of which convenient kinds have been described by Rutherford (Phil. Trans. Ed. iii. 245). That for ascertaining the most intense cold is made with alcohol, and the bulb is bent at a right angle to the stem, so that the latter may conveniently be placed in a horizontal position. In the spirit is immersed a cylindrical piece of black enamel, of such size as to move freely within the tube. In order to make an observation, the enamel should be brought down to the surface of the spirit, an object easily effected by slight percussion while the bulb is inclined upwards. When the thermometer sinks by exposure to cold, the enamel likewise retreats towards the bulb, owing to its adhesion to the spirit; but, on expanding, the spirit passes readily beyond the enamel, leaving it at the extreme point to which it had been conveyed by the previous contraction. For registering the highest temperature, a common mercurial thermometer of the same form as the preceding is employed, having a small cylindrical piece of black enamel at the surface of the mercury. When the mercury expands, the enamel is pushed forward; and as the stem of the thermometer is placed horizontally, it does not recede when the mercury contracts, but remains at the spot to which it had been conveyed by the previous dilatation. The enamel is easily restored to the surface of the mercury by slight percussion while the bulb is inclined downwards; but this should be performed with care, lest the enamel, in falling abruptly, should interrupt the continuity of the mercurial column. The risk of this accident is lessened by putting some pure naphtha in the tube beyond the mercury, and its presence is likewise of use in preventing the oxidation of the mercury. The above description applies to an improvement on Rutherford's thermometer, made by Adie of Edinburgh.

Though the thermometer is one of the most valuable instruments of philosophical research, it must be confessed that the sum of information which it conveys is very small. It does indeed point

out a difference in the temperature of two or more substances with great nicety; but it does not indicate how much heat any body contains. It does not follow, because the thermometer stands at the same elevation in any two bodies, that they contain equal quantities of heat; nor is it right to infer that the warmer possesses more of this principle than the colder. The thermometer gives the same kind of information which may be discovered, though less accurately, by the feelings; it recognizes in bodies that state alone which affects the senses with an impression of heat or cold,—the condition expressed by the word *temperature*. All we learn by this instrument is, whether the temperature of one body is greater or less than that of another; and if there is a difference, it is expressed numerically, namely, by the degrees of the thermometer. But it must be remembered that these degrees are parts of an arbitrary scale, selected for convenience, without any reference whatever to the actual quantity of heat present in bodies.

A little reflection will evince the propriety of these remarks. If two glasses of unequal size be filled with water just taken from the same spring, the thermometer will stand in each at the same height, though their quantities of heat are certainly unequal. This observation naturally suggests the inquiry, whether different kinds of substances, whose temperatures as estimated by the thermometer are the same, contain equal quantities of heat,—if, for example, a pound of iron contains as much heat as a pound of water or mercury. The foregoing remark shows that equality in temperature is not necessarily connected with equality in quantity of heat; and the inference has been amply confirmed by experiment. If equal quantities of water are mixed together, one portion being at 100° and the other at 50° , the temperature of the mixture will be the arithmetical mean or 75° ; that is, the 25 degrees lost by the warm water will exactly suffice to heat the cold water by the same number of degrees. It is hence inferred, that equal weights or measures of water of the same temperature contain equal quantities of heat; and the same is found to be true of other bodies. But if equal weights or equal bulks of *different* substances are employed, the result will be different. Thus if a pint of mercury at 100° be mixed with a pint of water at 40° , the mixture will have a temperature of 60° , so that the 40 degrees lost by the former, heated the latter by 20 degrees only; and when, reversing the experiment, the water is at 100° and the mercury at 40° , the mixture will be at

80°, the 20 degrees lost by the former causing a rise of 40 in the latter. The fact is still more strikingly displayed by substituting equal weights for measures. For instance, on mixing a pound of mercury at 160° with a pound of water at 40°, a thermometer placed in the mixture will stand at 45°; but if the mercury be at 40° and the water at 160°, the mixture will have a temperature of 155°. If water at 100° be mixed with an equal weight of spermaceti oil at 40°, the mixture will be found at 80°; and when the oil is at 100° and the water at 40°, the temperature of the mixture will be only 60°.

It appears from these facts, that the same quantity of heat imparts twice as high a temperature to mercury as to an equal volume of water; that a similar proportion is observed with respect to equal weights of spermaceti oil and water; and that the heat which gives 5 degrees to water will raise an equal weight of mercury by 115 degrees, being the ratio of 1 to 23. Hence if equal quantities of heat be added to equal weights of water, spermaceti oil, and mercury, their temperatures in relation to each other will be expressed by the numbers 1, 2, and 23; or, what amounts to the same, in order to increase the temperature of equal weights of those substances to the same extent, the water will require 23 times more heat than the mercury, and twice as much as the oil. The peculiarity exemplified by these substances, and which it would be easy to illustrate by other examples, was first noticed by Black. It is a law admitted to be universal, and may be thus expressed: that *equal* quantities of different bodies require *unequal* quantities of heat to heat them equally. This difference in bodies was expressed by Black by the term *capacity* for heat, a word apparently suggested by the idea that the heat present in any substance is contained within its pores, or in the spaces left between its particles, and that the quantity of heat is regulated by the size of the pores. And indeed at first view there appear sufficient grounds for this opinion; for it is observed, that very compact bodies have the smallest capacities for heat, and that the capacity of the same substance often increases as its density becomes less. But, as Black himself pointed out, if this were the real cause of the difference, the capacities of bodies for heat should be inversely as their densities. Thus, since mercury is $13\frac{1}{2}$ times denser than water, the capacity of the latter for heat ought to be only $13\frac{1}{2}$ times greater than the former, whereas it is 23 times as

great. Oil occupies more space than an equal weight of water, and yet the capacity of the latter for heat is double that of the former. The word capacity therefore is apt to excite a wrong notion, unless it be carefully borne in mind, that it is merely an expression of the fact without allusion to its cause; to avoid the chance of error from this source, the term *specific heat* has been proposed as a substitute for it, and is now very generally employed.

The singular fact of substances of equal temperature containing unequal quantities of heat naturally excites speculation about its cause, and various attempts have been made to account for it. The explanation deduced from the views of Black is the following. He conceived that heat exists in bodies in two opposite states: in one it is supposed to be in chemical combination, exhibiting none of its ordinary characters, and remaining as it were concealed, without evincing any signs of its presence; in the other, it is free and uncombined, passing readily from one substance to another, affecting the senses in its passage, determining the height of the thermometer, and, in a word, giving rise to all the phenomena which are attributed to this active principle.

Though it would be easy to start objections to this ingenious conjecture, it has the merit of explaining phenomena more satisfactorily than any view that has been proposed in its place. It is entirely consistent with analogy. For since heat is regarded as a material substance, it would be altogether anomalous were it not influenced, like other kinds of matter, by chemical affinity; and if this be admitted, it ought certainly, in combining, to lose some of the properties by which it is distinguished in its free state. According to this view it is intelligible how two substances, from being in the same condition with respect to free heat, may have the same temperature; and yet that their actual quantities of heat may be very different, in consequence of one containing more of that principle in a combined or latent state than the other. But in admitting the plausibility of this explanation, it is proper to remember that it is at present entirely hypothetical; and that the language suggested by an hypothesis should not be unnecessarily associated with the phenomena to which it owes its origin. Accordingly, the word *sensible* is better than *free heat*, and *insensible* preferable to *combined* or *latent heat*; for by such terms the fact

is equally well expressed, and philosophical propriety strictly preserved.

It is of importance to know the specific heat of bodies. The most convenient method of discovering it, is by mixing different substances together in the way just described, and observing the relative quantities of heat requisite for heating them by the same number of degrees. Thus the heat required to heat equal quantities of water, spermaceti oil, and mercury by one degree, is in the ratio of 23, 11.5, and 1, and therefore their specific heats are expressed by those numbers. Water is commonly one of the materials employed in such experiments, as it is customary to compare the sp. heat of other bodies with that of water.*

This method was first suggested by Black, and was afterwards practised to a great extent by Crawford and Irvine.† But the same knowledge may be obtained by reversing the process,—by noting the relative quantities of heat which bodies give out in cooling; for if water require 23 times more heat than mercury to raise its temperature by one or more degrees, it must also lose 23 times as much in cooling. The calorimeter, invented and employed by Lavoisier and Laplace, acts on this principle. The apparatus consists of a wire cage, suspended in the centre of a metallic vessel so much larger than itself, that an interval is left between them, which is filled with fragments of ice. The mode of estimating the quantity of heat which is emitted by a hot body placed in the wire cage, depends upon the fact, that ice cannot be heated beyond 32°; since every particle of heat which is then supplied is employed in liquefying it, without in the least affecting its temperature. If, therefore, a flask of boiling water be put

* A formula for such calculations is thus deduced:—Let w , t , and s be the weight, temperature, and specific heat of the warmer body; w' , t' , and s' the weight, temperature, and specific heat of the colder body; and θ the temperature of the mixture. Then the temperature lost by the warmer body will be expressed by $(t-\theta)$, and its actual loss of heat by $s \cdot (t-\theta) \cdot w$; while the temperature acquired by the colder body will be $(\theta-t')$, and the whole heat gained will be represented by $s' \cdot (\theta-t') \cdot w'$. As the heat gained by the one is equal to that lost by the other, it follows that $s \cdot (t-\theta) \cdot w = s' \cdot (\theta-t') \cdot w'$; and consequently $\frac{s}{s'} = \frac{(\theta-t') \cdot w'}{(t-\theta) \cdot w}$. In case of the weights being equal, or $w = w'$, then $\frac{s}{s'} = \frac{\theta-t'}{t-\theta}$; that is, for equal weights, the specific heats are inversely as the variations of temperature.

† Crawford on Animal Heat, and Irvine's Chemical Essays.

into the cage, it will gradually cool, the ice will continue at 32° , and a portion of ice-cold water will be formed; and the same change will happen when heated mercury, oil, or any other substance is substituted for the hot water. The sole difference will consist in the quantity of ice liquefied, which will be proportional to the heat lost by those bodies while they cool; so that their capacity is determined merely by measuring the quantity of water produced by each of them. This is done by allowing the water, as it forms, to run out of the calorimeter by a tube fixed in the bottom of it, and carefully weighing the liquid which issues.

There is one obvious source of fallacy in this mode of operating, against which it is necessary to provide a remedy: namely, the ice not only receives heat from the substance in the central cage, but must also receive it from the air of the apartment in which the experiment is conducted. This inconvenience is avoided by surrounding the whole apparatus by a larger metallic vessel of the same form as the smaller one, and of such a size that a certain space is left between them, which is to be filled with pounded ice or snow. No external heat can now penetrate to the inner vessel; because all the heat derived from the apartment is absorbed by the outer one, and is employed, not in elevating its temperature, but in dissolving the pounded ice within it.

In spite of this precaution the calorimeter is not a correct instrument. The fragments of ice in contact with each other retain by capillary attraction more or less water, the quantity of which varies as the fragments change their figure by fusion during an experiment. Hence the water which issues, cannot be relied on as representing the quantity of ice fused. Actual cavities wherein water might lodge in considerable quantity, might also be produced. But the principle by which the calorimeter measures heat, namely, the conversion of ice at 32° into water at 32° , is unexceptionable.

The determination of the sp. heat of gaseous substances is a problem of importance, and has occupied the attention of several experimenters of great science and practical skill; but the inquiry is beset with so many difficulties that, in spite of the talent which has been devoted to it, our best results can be viewed as approximations only, requiring to be corrected by future research. Crawford, to whom we are indebted for the first elaborate investigation of the subject, conducted his experiments in the following manner.

He obtained two copper vessels made as light as possible, and exactly of the same form, size, and weight: he exhausted one of them, and filled the other with the gas to be examined. They were next heated to the same extent by immersion in hot water, and then plunged into equal quantities of cold water of the same temperature. Each flask heated the water; but while the exhausted flask communicated solely the heat of the copper, the other gave out an equal quantity of heat from the metal of which it was made, together with that derived from the gas in its interior. The effect produced by the former deducted from that of the latter gave the heating power of the confined gas. By repeating the experiment with air and different gases, their comparative heating powers, or their sp. heats, were ascertained. But correct as is the leading principle on which these experiments were founded, the results are now universally admitted to be very wide of the truth, and therefore it can answer no useful purpose to cite them. The fallacy is attributable to the circumstance of the heat derived from the containing vessel being so great compared to that emitted by the confined gas, that the effect ascribed to the latter is confounded with, and materially influenced by, the unavoidable errors of manipulation.

The same subject was investigated by Lavoisier and Laplace by means of their calorimeter. A current of gas was transmitted in a serpentine tube through boiling water in order to be heated, and was then made to circulate within the calorimeter in a similar tube surrounded with ice. Its temperature in entering and quitting the calorimeter was ascertained by thermometers, and the heat lost by each gas was estimated by the quantity of ice liquefied. Their experiments are of course liable to the objections already made to the calorimeter; but a similar train of experiments, not exposed to this fallacy, was conducted in the year 1813 with extreme care by Delaroche and Bérard. (*An. de Chimie*, LXXXV. and *Annals of Phil.* II.) They transmitted known quantities of gas, heated to 212° , in an uniform current through the calorimeter; and, instead of ice, surrounded the serpentine tube with water, the temperature of which, as well as of the gas at its exit, was ascertained during the course of the process by delicate thermometers. By operating with a considerable quantity of gas, they avoided the error into which Crawford fell; and the experiments, though complicated and involving various sources of error, were conducted with such skill

and caution, that they inspired great confidence, and are still admitted to be more accurate than any which have been made on this difficult subject. Their results are contained in the following table; the sp. heat of the gases being referred to atmospheric air as unity in the two first columns, and to water in the third.

Names of Substances.	Under equal Volumes and constant Pressure.	Under equal Weights.
Atmospheric air . .	1·0000	1·0000 . . 0·2669
Hydrogen gas . . .	0·9033	12·3400 . . 3·2936
Oxygen gas . . .	0·9765	0·8848 . . 0·2361
Nitrogen gas . . .	1·0000	1·0318 . . 0·2754
Nitrous oxide gas . .	1·3503	0·8878 . . 0·2369
Olefiant gas . . .	1·5530	1·5763 . . 0·4207
Carbonic oxide gas . .	1·0340	1·0805 . . 0·2884
Carbonic acid gas . .	1·2583	0·8280 . . 0·2210
Water 1·0000
Aqueous vapour 0·8470

Some experiments by Clement and Desormes (*Journal de Physique*, LXXXIX. 320, 1819) were confirmatory of the foregoing results; and Dalton, in the second volume of his *Chemical Philosophy*, page 282, states that he has repeated the experiment of Delaroche and Bérard on the sp. heat of atmospheric air, and is convinced of their estimate being very near the truth. But the accuracy of their results has been questioned by others, and some of the objections are by no means deficient in force. One of these was stated by Haycraft in the *Edinburgh Phil. Trans.* for 1824, namely, that the gases were employed in a moist instead of a dry state, a circumstance which would doubtless in some measure modify the result; and others have been mentioned by De la Rive and Marcet (*An. de Ch. et Ph.* xxxv. 5, and xli. 78). For example, the precise temperature of the gases used in their experiments was not ascertained in an unexceptionable manner; because a thermometer surrounded by gaseous matter is affected, not only by contact with the gas itself, but likewise by the radiant heat emitted or absorbed by the containing vessel. It is also to be remarked that the heated gases, in passing through the calorimeter, diminished in volume in proportion as they cooled. Now it is found invariably that whenever the bulk of a gas is diminished, a certain portion of insensible heat becomes sensible; so that in the

experiments of Delaroche and Bérard, the heating influence of the gases was a complex phenomenon, partly dependent on the heat lost in cooling, and partly on that developed by the accompanying diminution in volume. This last source of heat ought to have been avoided, and in the experiments of Crawford it was so; for the heated gases with which he operated, being confined in a close vessel, underwent no change of volume while they cooled, though of course their elasticity was thereby diminished.

These considerations led to the experiments of De la Rive and Marcet, who confined the gases in a thin globe of glass, and estimated the temperature, not by a thermometer, but by the elastic force communicated by the heat, according to the law of Dalton and Gay-Lussac already mentioned (p. 34). The glass vessel was placed in the centre of a very thin copper globe, the inner surface of which was made to radiate freely by a coating of lamp-black, and the air between it and the glass globe was withdrawn by an air-pump. The whole apparatus, being brought to the temperature of 68° , was immersed during exactly five minutes in water kept steadily at 86° ; and the heat imparted to the copper was radiated from its inner surface, and thus reached the glass globe in the centre. By always operating exactly in the same manner, it was conceived that the same volume of each gas would receive equal quantities of heat in equal times; and that from the temperature thus communicated to each, its specific heat might be inferred. In two sets of experiments thus conducted, they found that each gas acquired the same elasticity, or was heated to the same degree; and thence they inferred that gases in general, for equal volumes and pressures, have the same sp. heat. They also operated with the same gas at different densities; and concluded that the sp. heat of each gas, for equal volumes, diminishes slowly as its density decreases.

In the *An. de Ch. et Ph.* xli. 113, Dulong has published some critical remarks on these experiments. He argues, in the first place, that the quantity of gas employed was so small, that any effect arising from a difference in sp. heat could not be appreciated. He contends, further, that the temperature acquired by a gas in such experiments is not influenced by its sp. heat only, but in part by the relative facility with which heat is transmitted through the gas. It has been already observed that heat is conducted by gaseous matter with extreme slowness, but is rapidly

diffused through it in consequence of the mobility of its particles. Now gases differ considerably under this point of view. Hydrogen acquires the temperature of a hot body placed in it much more rapidly than carbonic acid; and therefore, were the same volume of these gases exposed for an equal short period to equal sources of heat, the former would acquire a higher temperature simply from its conveying heat more readily. The validity of these strictures can scarcely, I apprehend, be denied. It may therefore be inferred, that the sp. heats of the gases are not yet accurately known, and that the numbers stated by Delaroche and Bérard are probably the best approximations hitherto published.

An elegant method of estimating the sp. heats of gases was founded by Dulong on La Place's formula for calculating the velocity of sound. This formula is indeed admitted as exact by the highest authorities; but as I entertain much doubt of its accuracy, I forbear to give Dulong's results obtained through its means, and simply refer to his essay (*An. de Ch. et Ph.* xli. 113). The theoretical reader may also consult the ingenious formula lately given by Apjohn for calculating sp. heats, founded on his method of finding the relation between the dew-point and the indications of the wet-bulb hygrometer. The accuracy of his method has scarcely as yet been sufficiently tested for inspiring full confidence in the results of the calculation. (*Phil. Mag. & An.* vii. 385, and viii. 21.)

The circumstances which merit particular notice, concerning the sp. heats of bodies, may be arranged under the eight following heads:—

1. Every substance has a sp. heat peculiar to itself; whence it follows, that a change of composition will be attended by a change of sp. heat.

2. The sp. heat of a body varies with its form. A solid has a smaller sp. heat than the same substance when in the state of a liquid; the sp. heat of water, for instance, being 9 in the solid state, and 10 in the liquid. Whether the same weight of a body has a greater sp. heat in the solid or liquid form than in that of vapour, is a circumstance not yet decided. The only experiments in point are those of Crawford, and Delaroche and Bérard. The former estimated the sp. heat of vapour at 1.55, and the French philosophers at 0.847, compared to that of water as unity; nor is

it possible to say which of these widely discordant results is nearer the truth, as neither can be relied on with confidence.

3. When a given weight of any gas is made to vary in density and volume while its elasticity is unchanged, as when air confined in a tube over mercury is heated and suffered to expand without variation of pressure, the sp. heat is believed to remain constant. Gaseous matter, being free from the disturbing agency of cohesion, is very equably influenced by heat: according to our best observations, equal increments of heat, when the elasticity is constant, give rise both to equal increments of temperature and equal expansions.

4. Of the sp. heats of equal volumes of the same gas at a varying density and elasticity, as when air is forced into a bottle with different degrees of force, nothing certain has been established; for the experiments of De la Rive and Marcet, above described, have led to no decisive conclusion.

5. The sp. heats of equal weights of the same gas vary as the density and elasticity vary. Thus, when 100 measures of air expand by diminished pressure to 200 measures, its sp. heat is increased; and when the same quantity of air is compressed into the space of 50 measures, its sp. heat is diminished. The exact rate of increase is unknown; but, according to Delaroche and Bérard, the ratio is less rapid than the diminution in density; that is, the sp. heat of any gas being 1, it is not 2, but between one and two, when its volume is doubled.

6. The sp. heats of solids and liquids were formerly thought, especially by Crawford and Irvine, to be constant at all temperatures, so long as they suffer no change of form or composition. Dalton, however, (*Chemical Philosophy*, part I. p. 50,) endeavours to show that the sp. heats of such bodies are greater in high than at low temperatures; and Petit and Dulong, in the essay already quoted, have proved it experimentally with respect to several of them. Thus the mean sp. heat of iron between

0° C and	.	100° Cent.	is	0.1098
0° C	.	200° C	.	0.1150
0° C	.	300° C	.	0.1218
0° C	.	350° C	.	0.1255

and the same is true of the substances contained in the following table.

	Mean Sp. Heat between 0° and 100° C.	Mean Sp. Heat between 0° and 300° C.
Mercury 0·0330 0·0350
Zinc 0·0927 0·1015
Antimony 0·0507 0·0549
Silver 0·0557 0·0611
Copper 0·0949 0·1013
Platinum 0·0355 0·0355
Glass 0·1770 0·1900

It is difficult to determine whether the increased sp. heat observed in solids and liquids at high temperatures is owing to the accumulation of heat within them, or to their dilatation. It is ascribed in general to the latter, and I believe correctly; because the expansion and contraction of gases by change of pressure, without the aid of heat, is attended with corresponding changes of sp. heat.

7. Change of sp. heat always occasions a change of temperature. Increase in the former is attended by diminution of the latter; and decrease in the former, by increase of the latter. Thus when air, confined within a flaccid bladder, is suddenly dilated by means of the air-pump, a thermometer placed in it will indicate the production of cold. On the contrary, when air is compressed, the corresponding diminution of its sp. heat gives rise to increase of temperature; nay, so much heat is evolved when the compression is sudden and forcible, that tinder may be kindled by it. The explanation of these facts is obvious. In the first case, a quantity of heat becomes insensible, which was previously in a sensible state; in the second, heat is evolved, which was previously latent.

8. An important relation between the sp. heats of some elementary substances and their equivalents was discovered by Dulong and Petit, namely, that the product of the sp. heat of each element by the weight of its atom is a constant quantity. This relation, if general, would be of great interest, as leading directly to the inference that the atoms of elementary substances are associated with equal quantities of heat, and enabling chemists to calculate either the sp. heats of elements from their equivalents, or conversely their equivalents from their sp. heats. (An. de Ch. et Ph. x. 403.) The relation above alluded to was exemplified by Dulong and Petit by a table similar to the subjoined.

	Specific Heat.	Relative Weights of Atoms.	Product of the Sp. Heat of each element by the weight of its atom.
Lead	0.0293	× 103. 6	= 3.0353
Tin	0.0514	× 57. 9	= 2.9760
Zinc	0.0927	× 32. 3	= 2.9942
Tellurium	0.0912	× 32. 3	= 2.9457
Copper	0.0949	× 31. 6	= 2.9988
Nickel	0.1035	× 29. 5	= 3.0532
Iron	0.1100	× 28	= 3.0800
Sulphur	0.1880	× 16. 1	= 3.0268
Platinum	0.0355	× 98. 8	= 3.3098
Bismuth	0.0288	× 71	= 2.0448
Cobalt	0.1498	× 29. 5	= 4.4191
Arsenic	0.081	× 37. 7	= 3.0537
Carbon	0.25	× 6.12	= 1.5300
Iodine	0.089	× 126. 3	= 11.2407
Phosphorus	0.385	× 15. 7	= 6.0445
Mercury	0.0330	× 202	= 6.6660
Silver	0.0557	× 108	= 6.0156
Gold	0.0298	× 199. 2	= 5.9361

It will be observed on inspecting the last column of the table, that the product of the sp. heat into the equivalent is very nearly 3 for the first nine substances. Platinum deviates visibly from the law; and bismuth, cobalt, and iodine, strikingly. The four last elements would nearly coincide with the law, were their respective equivalents estimated at half the numbers given in the tables, as would carbon were its equivalent doubled. These coincidences are too close and numerous to arise from chance, and justify a belief in the law having a real foundation dependent on the connexion between heat and the elementary particles of matter. The researches of Avogadro and Neumann give additional weight to this opinion by tracing the same law in many compound bodies, those compounds alone being compared together whose atomic constitution is similar (An. de Ch. et Ph. LV. 80, and LVII. 113; and Pog. An. XXIII. 1). Dalton, in his Chemical Philosophy, ii. 293, contends that the law cannot be true; since, as Dulong and Petit have shown, the sp. heat of a substance is not constant, but varies both from a change of form, and even with variation of temperature without change of form. To the latter part of the criticism Dulong and Petit are certainly exposed; but they have anticipated the former by remarking, that the law is not affected by change of form, provided the substances compared are taken in the same state. Future observation must decide on the validity of this position.

ON LIQUEFACTION.

All bodies are solid, liquid, or gaseous; and the form they assume depends on the relative intensity of cohesion and repulsion. Should the repulsive force be comparatively feeble, the particles will adhere so firmly together, that they cannot move freely upon one another, thus constituting a solid. If cohesion is so far counteracted by repulsion, that the particles move on each other freely, a liquid is formed. And should the cohesive attraction be entirely overcome, so that the particles not only move freely on each other, but would, unless restrained by external pressure, separate from one another to an almost indefinite extent, an æriform substance will be produced.

Now the property of repulsion is manifestly owing to heat; and as it is easy within certain limits to increase or diminish the quantity of this principle in any substance, it follows that the form of bodies may be made to vary at pleasure: that is, by heat sufficiently intense every solid may be converted into a fluid, and every fluid into vapour. This inference is so far justified by experience, that it may safely be considered as a law. The converse ought also to be true; and, accordingly, several of the gases have already been condensed into liquids by means of pressure, and liquids have been solidified by cold. The temperature at which liquefaction takes place is called the melting point, or point of fusion; and that at which liquids solidify, their point of congelation. Both these points are different for different substances, but uniformly the same, under similar circumstances, in the same body.

The most important circumstance relative to liquefaction is Black's discovery that a large quantity of heat disappears, or becomes insensible to the thermometer, during the process. If a pound of water at 32° be mixed with a pound of water at 172° , the temperature of the mixture will be intermediate between them, or 102° . But if a pound of water at 172° be added to a pound of ice at 32° , the ice will quickly dissolve, and on placing a thermometer in the mixture, it will be found to stand, not at 102° , but at 32° . In this experiment, the pound of hot water, which was originally at 172° , actually loses 140 degrees of heat, all of which enters into the ice, and causes its liquefaction, but without affecting its temperature; whence it follows that a quantity of heat becomes insensible during the melting of ice, sufficient to raise the temperature of an equal weight of water by 140 degrees. This explains the well-

known fact, on which the graduation of the thermometer depends, —that the temperature of melting ice or snow never exceeds 32° . All the heat which is added becomes insensible, till the liquefaction is complete.

The loss of sensible heat which attends liquefaction seems essentially necessary to the change, and for that reason is frequently called the *heat of fluidity*. The actual quantity of heat required for this purpose varies with the substance, as is proved by the following results obtained by Irvine. The degrees indicate the extent to which an equal weight of each material may be heated by the heat of fluidity which is proper to it.

Heat of Fluidity.		Heat of Fluidity.	
Sulphur	$143^{\circ}68\text{F.}$	Zinc	493°
Spermaceti	145°	Tin	500°
Lead	162°	Bismuth	550°
Bees-wax	175°		

As so much heat disappears during liquefaction, it follows that heat must be evolved when a liquid passes into a solid. This may easily be proved. The temperature of water in the act of freezing remains at 32° , though exposed to an atmosphere in which the thermometer is at zero. That the water under such circumstances may preserve its temperature, heat must be supplied as fast as it is abstracted; and it is obvious that the only source of supply is the heat of fluidity. Further, if pure recently boiled water be cooled very slowly, and kept very tranquil, its temperature may be lowered to 21° without any ice being formed; but the least motion causes it to congeal suddenly, and in doing so its temperature rises to 32° . (Blagden in Phil. Trans. 1788.)

The explanation which Black gave of these phenomena constitutes what is called his *doctrine of latent heat*, which was partially explained on a former occasion (page 46). He conceived that heat in causing fluidity loses its property of acting on the thermometer in consequence of combining chemically with the solid substance, and that liquefaction results, because the compound so formed does not possess that degree of cohesive attraction on which solidity depends. When a liquid is cooled to a certain point, it parts with its heat of fluidity, which is set free or becomes sensible, and the cohesion natural to the solid is restored. The same mode of reasoning was applied by Black to the conversion of liquids into vapours, a change during which a large quantity of heat disappears.

A different explanation of the phenomena was proposed by

Irvine. Observing that a solid has a smaller sp. heat than the same substance while liquid, he argued that this circumstance alone accounts for heat becoming insensible during liquefaction. For since the sp. heat of ice and water, or in other words, the quantity of heat required to raise their temperature by the same number of degrees, was found to be as 9 to 10, Irvine inferred that ice must contain one-tenth less heat than water of the same temperature, and that as this difference must be supplied to the ice when it is converted into water, the change must necessarily be accompanied with the disappearance of heat. Irvine applied the same argument to the liquefaction of all solids, and likewise to account for the heat which is rendered insensible during the formation of vapour.

Two objections may properly be urged against the opinion of Irvine. In the first place, no adequate reason is assigned for the liquefaction. It accounts for the disappearance of heat which accompanies liquefaction, but does not explain why the body becomes liquid; whereas the hypothesis of Black affords an explanation both of the change itself, and of the phenomena that attend it. But the second objection is still more conclusive. Irvine argued on the belief that a liquid has in every case a greater sp. heat than when solid; and though this point has not been demonstrated in a manner entirely decisive, yet from the experiments hitherto made, it appears that liquids in general have greater sp. heats than solids, and that therefore Irvine's assumption is probably correct in regard to them. In like manner he believed vapours to have greater sp. heats than the liquids that yield them; and his opinion was supported by the experiments of Crawford on the sp. heats of water and watery vapour. But no reliance can be placed on the researches of Crawford; not only because his result is so different from that obtained by Delaroche and Bérard, but because all his other experiments on the sp. heats of elastic fluids are decidedly erroneous (page 49). Indeed from the fact of most gases having smaller sp. heats than liquids, it is probable that the sp. heats of elastic fluids in general are inferior to those of the liquids from which they are derived. The disappearance of heat during vaporization is not explicable on the views of Irvine; it is necessary to employ the theory of Black to account for that change, and therefore the same doctrine should be applied to the analogous phenomenon of liquefaction.

In speculating on the cause of the sp. heats of bodies at page 46,

I had recourse to the doctrine of latent or combined heat. Black restricted the use of this hypothesis to explain the phenomena of liquefaction and vaporization ; but I apprehend it may be applied without impropriety to all cases where heat passes from a sensible to an insensible state. That this may happen, when heat enters a body, without change of form, is easily demonstrated. Thus, in order to raise an equal weight of water and mercury by the same number of degrees, it is necessary to add 23 times as much heat to the water as to the mercury ; a fact which proves a quantity of heat to become insensible to the thermometer when the temperature of water is raised by one degree, just as happens when ice is converted into water, or water into vapour. The phenomena are in this point of view identical ; and, therefore, the same mode of reasoning by which one of them is explained, may be employed to account for the other.

The loss of sensible heat in liquefaction is the basis of many artificial processes for producing cold, all of which are founded on the principle of liquefying solid substances without supplying heat. The heat of fluidity being then derived from that which had previously existed within the solid itself in a sensible state, the temperature necessarily falls. The degree of cold thus produced depends upon the quantity of heat which disappears ; and this again is dependent on the quantity of solid matter liquefied, and on the rapidity of liquefaction.

The most common method of producing cold is by mixing together equal parts of snow and salt. The salt causes the snow to melt by reason of its affinity for water, and the water dissolves the salt ; so that both of them become liquid. The cold thus generated is 32 degrees below the temperature of freezing water ; that is, a thermometer placed in the mixture would stand at zero. This is the way originally proposed by Fahrenheit for determining the commencement of his scale.

Any other substances which have a strong affinity for water may be substituted for the salt ; and those have the greatest effect in producing cold whose affinity for that liquid is greatest, and which consequently produce the most rapid liquefaction. Crystallized chloride of calcium, proposed by Löwitz, is by far the most convenient in practice. It may be made by dissolving marble in hydrochloric acid, and concentrating the solution by evaporation, till, upon letting a drop of it fall upon a cold saucer, it becomes a solid

mass. It should then be withdrawn from the fire, and when cold be speedily reduced to a fine powder. From its extreme deliquescence it must be preserved in well-stopped vessels. The following table by Mr. Walker contains the best proportions for producing intense cold. (Phil. Trans. 1801.)

FRIGORIFIC MIXTURES WITH SNOW.*

MIXTURES. Parts by Weight.	Thermometer sinks.	Degree of Cold produced.
Sea-salt 1 Snow 2	From any Temperature { to -5° to -12° to -18° to -25°	
Sea-salt 2 Hydrochlorate of Ammonia 1 Snow 5		
Sea-salt 10 Hydrochlorate of Ammonia 5 Nitrate of Potassa . . . 5 Snow 24		
Sea-salt 5 Nitrate of Ammonia . . . 5 Snow 12		
Diluted Sulphuric Acid† 2 Snow 3	from $+32^{\circ}$ to -23°	55 degrees.
Concentrated Hydrochloric Acid 5 Snow 8	from $+32^{\circ}$ to -27°	59
Concentrated Nitrous Acid 4 Snow 7	from $+32^{\circ}$ to -30°	62
Chloride of Calcium . . . 5 Snow 4	from $+32^{\circ}$ to -40°	72
Crystallized Chloride of Calcium 3 Snow 2	from $+32^{\circ}$ to -50°	82
Fused Potassa 4 Snow 3	from $+32^{\circ}$ to -51°	83

Freezing mixtures are also made by the rapid solution of salts, without the use of snow or ice: the following table, by Walker, includes the most important of them. The salts must be finely powdered and dry. (Phil. Trans. 1795.)

* The snow should be freshly fallen, dry, and uncompressed. If snow cannot be had, finely pounded ice may be substituted for it.

† Made of strong acid, diluted with half its weight of snow or distilled water.

MIXTURES. Parts by Weight.	Temperature falls.	Degree of Cold produced.
Hydrochlorate of Ammonia 5 Nitrate of Potassa . . 5 Water . . . 16	from $+50^{\circ}$ to $+10^{\circ}$	40 degrees.
Hydrochlorate of Ammonia 5 Nitrate of Potassa . . 5 Sulphate of Soda . . 8 Water . . . 16	from $+50^{\circ}$ to $+4^{\circ}$	46
Nitrate of Ammonia . . 1 Water . . . 1	from $+50^{\circ}$ to $+4^{\circ}$	46
Nitrate of Ammonia . . 1 Carbonate of Soda . . 1 Water . . . 1	from $+50^{\circ}$ to -7°	57
Sulphate of Soda . . 3 Diluted Nitrous Acid* 2	from $+50^{\circ}$ to -3°	53
Sulphate of Soda . . 6 Hydrochlorate of Ammonia 4 Nitrate of Potassa . . 2 Diluted Nitrous Acid 4	from $+50^{\circ}$ to -10°	60
Sulphate of Soda . . 6 Nitrate of Ammonia . . 5 Diluted Nitrous Acid . 4	from $+50^{\circ}$ to -14°	64
Phosphate of Soda . . 9 Diluted Nitrous Acid . 4	from $+50^{\circ}$ to -12°	62
Phosphate of Soda . . 9 Nitrate of Ammonia . . 6 Diluted Nitrous Acid . 4	from $+50^{\circ}$ to -21°	71
Sulphate of Soda . . 8 Hydrochloric Acid . . 5	from $+50^{\circ}$ to 0°	50
Sulphate of Soda . . 5 Diluted Sulphuric Acid† 4	from $+50^{\circ}$ to $+3^{\circ}$	47

These artificial processes for generating cold are much more effectual when the materials are previously cooled by immersion in other frigorific mixtures. One would at first suppose that an unlimited degree of cold might be thus produced; but it is found that when the difference between the mixture and the air becomes very great, the communication of heat from one to the other becomes so rapid, as to put a limit to the reduction. The greatest cold produced by Walker did not exceed 100 degrees below the zero of Fahrenheit.

Though we shall probably never succeed in depriving any sub-

* Composed of fuming nitrous acid 2 parts in weight, and one of water; the mixture being allowed to cool before being used.

† Composed of equal weights of strong acid and water, being allowed to cool before use.

stance of all its heat, bodies doubtless contain a certain definite quantity of this principle, and various attempts have been made to calculate its amount. Irvine made the calculation by assuming the actual quantities of heat in bodies to be proportional to their sp. heats, and their sp. heats to be constant so long as their form did not change. Thus, as the sp. heats of ice and water are as 9 to 10, it followed on his hypothesis, that ice contains 1-10th less heat than water of the same temperature. But this tenth, which is the heat of fluidity, was found by Black to be 140 degrees; and hence Irvine inferred that water at 32° contains 10 times 140 or 1400 degrees of heat.

To be satisfied that such calculations cannot be trusted, it is sufficient to know that the estimates made by different chemists respecting the absolute quantity of heat in water vary from 900 to nearly 8000.* Besides, did even the estimates agree with each other, the principle of the calculation would still be unsatisfactory; for, in the first place, there is no proof that the quantities of heat in bodies are in the ratio of their sp. heats; and, *secondly*, the assumption that the sp. heat of a body is the same at all temperatures, so long as it does not experience a change of form, has been proved to be erroneous by the experiments of Dulong and Petit.

VAPORIZATION.

*Aëri*form substances are commonly divided into vapours and gases. The former are characterised by their ready conversion into liquids or solids, either by a moderate increase of pressure, the temperature at which they were formed remaining the same, or by a moderate diminution of that temperature, without change of pressure. Gases, on the contrary, retain their elastic state more obstinately: they are always gaseous at common temperatures; and, with one or two exceptions, cannot be made to change their form, unless by being subjected to much greater pressure than they are naturally exposed to. Several of them, indeed, have hitherto resisted every effort to compress them into liquids. The only difference between gases and vapours is in the relative forces with which they resist condensation.

Heat is the cause of vaporization as well as of liquefaction. A

* Dalton's New System of Chemical Philosophy.

sufficiently intense heat would doubtless convert every liquid and solid into vapour. Some bodies, however, resist the strongest heat of our furnaces without vaporizing. These are said to be *fixed* in the fire; those which, under the same circumstances, are converted into vapour, are called *volatile*.

The disposition of various substances to yield vapour is very different; and the difference depends doubtless on the relative power of cohesion with which they are endowed. Fluids, in general, are more easily vaporized than solids, as would be expected from the weaker cohesion of the former. Some solids, such as arsenic and sal-ammoniac, pass at once into vapour without being liquefied; but most of them become liquid before assuming the elastic condition.

Vapours occupy more space than the substances from which they were produced. Gay-Lussac found that water, in passing from its point of greatest density into vapour, expands to 1696 times its volume, alcohol to 659 times, and ether to 443 times, each vapour being at 212° and under a pressure of 29.92 inches of mercury. This shows that vapours differ in density. Watery vapour is lighter than air at the same temperature and pressure in the ratio of 1000 to 1604; or the sp. gr. of air being 1000, that of watery vapour is 625. The vapour of alcohol, on the contrary, is half as heavy again as air; and that of ether is more than twice and a half as heavy. As alcohol boils at a lower temperature than water, and ether than alcohol, it was conceived that the density of vapours might be in the direct ratio of the volatility of the liquids which produced them. But Gay-Lussac has shown that this law is not general; since bi-sulphuret of carbon boils at a higher temperature than ether, and nevertheless it yields a heavier vapour.

The dilatation of vapours by heat was found by Gay-Lussac to follow the same law as gases; that is, for every degree of Fahrenheit, they increase by $\frac{1}{480}$ th of the volume they occupied at 32° . But the law does not hold unless the quantity of vapour continue the same. If the increase of temperature cause a fresh portion of vapour to rise, then the expansion will be greater than $\frac{1}{480}$ th for each degree; because the heat not only dilates the vapour previously existing to the same extent as if it were a real gas, but augments its bulk by adding a fresh quantity of vapour. The contraction of a vapour on cooling will likewise deviate from the above law, whenever the cold converts any of it into a liquid; an effect which

must happen, if the space had originally contained its maximum of vapour. These circumstances should be held in view in estimating the influence of heat over the bulk of vapours. The formula of page 35, when applied to vapours, often leads to a result which would be true of any gas, but which may be untrue for vapour by reason of its light condensibility. Thus, 100 measures of steam at 212° and 30 inches bar. would *theoretically* occupy nearly 73 measures at 32° and at the same pressure; but this estimate is *practically* untrue, because under the conditions specified water cannot exist in the state of vapour.

Vapours vary in volume under varying pressure according to the same law as gases, provided always that the gaseous state is preserved. This law, which was discovered by Boyle and Mariotte, and is more fully explained in the section on atmospheric air, merely expresses the fact that the volume of gaseous substances at a constant temperature is inversely as the pressure to which they are subject. If 100 measures of steam at 212° , and under the atmospheric pressure, be exposed to a pressure of two atmospheres, the vapour will be entirely condensed, affording an instance of failure in the law in consequence of the gaseous state being entirely destroyed; but if the pressure be halved instead of doubled, the 100 measures retaining the gaseous form, and hence acting as a gas, will expand to 200 measures. In fact, if v be the volume corresponding to any pressure— p , expressed in inches of mercury, we shall have $\frac{v}{100} = \frac{30}{p}$; and hence $v = 100 \times \frac{30}{p}$. This formula gives the change of volume due to a change of pressure from 30 to p , the temperature being supposed at 212° in both cases.—To render the preceding paragraph intelligible to the young student, it should be mentioned that pressure, in reference to the volume of gaseous matter, is usually expressed by the length of a column of mercury: a mercurial column, 30 inches in length, presses on a given surface with the same force as the atmosphere in its ordinary state; and hence a 60-inch column is equal to two atmospheres, 15 inches to half an atmosphere, and one inch to 1-30th of the atmospheric pressure.

Vaporization is conveniently studied under two heads,—*Ebullition* and *Evaporation*. In the first, the production of vapour is so rapid that its escape gives rise to a visible commotion in the liquid; in the second, it passes off quietly and insensibly.

EBULLITION.

The temperature at which vapour rises with sufficient freedom for causing the phenomena of ebullition, is called the *boiling point*. The heat requisite for this effect varies with the nature of the fluid. Thus, sulphuric ether boils at 96° , alcohol at 176° , and pure water at 212° ; while oil of turpentine must be raised to 316° , and mercury to 662° , before either exhibits marks of ebullition. The boiling point of the same liquid is constant, so long as the necessary conditions are preserved; but it is liable to be affected by several circumstances. The nature of the vessel has some influence upon it. Thus Gay-Lussac observed that pure water boils precisely at 212° in a metallic vessel, and at 214° in one of glass, owing apparently to its adhering to glass more powerfully than to a metal. It is likewise affected by the presence of foreign particles: when a few iron filings are thrown into water boiling in a glass vessel, its temperature quickly falls from 214° to 212° , and remains stationary at the latter point. But the circumstance which has the greatest influence over the boiling point of liquids is variation of pressure. All bodies upon the earth are constantly exposed to considerable pressure; for the atmosphere itself presses with a force equivalent to a weight of 15 pounds on every square inch of surface. Liquids are exposed to this pressure as well as solids, and their tendency to take the form of vapour is very much counteracted by it. In fact, they cannot enter into ebullition at all, till their particles have acquired such elastic force as enables them to overcome the pressure upon their surfaces; that is, till they press against the atmosphere with the same force as the atmosphere against them. Now the atmospheric pressure is variable, and hence it follows that the boiling point of liquids must also vary.

The pressure of the atmosphere is equal to a weight of 15 pounds on every square inch of surface, when the barometer stands at 30 inches, and then only does water boil at 212° . If the pressure be less, that is, if the barometer fall below 30 inches, then the boiling point of water and every other liquid will be lower than usual; or if the barometer rise above 30 inches, the temperature of ebullition will be proportionally increased. On this account water boils at a lower temperature on the top of a hill than in the valley beneath it; for as the column of air diminishes in length as we ascend, its pressure must likewise suffer a proportional diminution.

The ratio between the depression of the boiling point, and the diminution of the atmospheric pressure is so exact, that it has been proposed as a method for determining the heights of mountains. An elevation of 530 feet makes a diminution of one degree. (Wallaston in Phil. Trans. for 1817.)

The influence of the atmosphere over the point of ebullition is best shown by removing its pressure altogether. Robison found that fluids boil *in vacuo* at a temperature 140° degrees lower than in the open air (Black's Lectures, 1. 151). Thus water boils *in vacuo* at 72°, alcohol at 36°, and ether at —44°. This proves that a liquid is not necessarily hot, because it boils. The heat of the hand is sufficient to make water boil in a vacuum, as is exemplified by the common pulse-glass; and ether, under the same circumstances, will enter into ebullition, though its temperature be low enough for freezing mercury.

Water cannot be heated under common circumstances beyond 212°, because it then acquires such expansive force as enables it to overcome the atmospheric pressure, and fly off in the form of vapour. But if subjected to sufficient pressure, it may be heated to any extent without boiling. This is best done by heating water while confined in a strong copper vessel, called Papin's Digester. In this apparatus, on the application of heat, a large quantity of vapour collects above the water, and checks ebullition by the pressure which it exerts upon the surface of the liquid. There is no limit to the degree to which water may thus be heated, provided the vessel is strong enough to confine the vapour; but the expansive force of steam under these circumstances is so enormous as to overcome the greatest resistance.

In estimating the power of steam it should be remembered that vapour, if separated from the liquid which produced it, does not possess greater elasticity than an equal quantity of air. If, for example, the digester were full of steam at 212°, no water in the liquid state being present, it might be heated to any degree, even to redness, without danger of bursting. But if water be present, then each addition of heat causes a fresh portion of steam to rise, which adds its own elastic force to that of the vapour previously existing; consequently an excessive pressure is soon exerted against the inside of the vessel. Robison (Brewster's edition of his works, p. 25) found that the tension of steam is equal to two atmospheres at 244°, and to three at 270°. The results of Southern's experiments, given in the same volume, fix upon 250·3° as the temperature of

which steam has the force of two atmospheres, on $293\cdot4^{\circ}$ for four, and $343\cdot6^{\circ}$ for eight atmospheres.

This subject has been examined by a commission appointed by the Parisian Academy of Sciences, and Dulong and Arago took a leading part in the inquiry. The results, which are given in the following table, were obtained by experiment up to a pressure of 25 atmospheres, and at higher pressures by calculation. (Brande's Journal, N. S. viii. 191.)

Elasticity of the vapour, taking atmospheric press. as unity.	Temperature according to Fahrenheit.	Elasticity of the vapour, taking atmospheric press. as unity.	Temperature according to Fahrenheit.
1	212	13	380·66
$1\frac{1}{2}$	233·96	14	386·94
2	250·52	15	392·86
$2\frac{1}{2}$	263·84	16	398·48
3	275·18	17	403·82
$3\frac{1}{2}$	285·08	18	408·92
4	293·72	19	413·78
$4\frac{1}{2}$	300·28	20	418·46
5	307·5	21	422·96
$5\frac{1}{2}$	314·24	22	427·28
6	320·36	23	431·42
$6\frac{1}{2}$	326·26	24	435·56
7	331·70	25	439·34
$7\frac{1}{2}$	336·86	30	457·16
8	341·78	35	472·73
9	350·78	40	486·59
10	358·88	45	491·14
11	366·85	50	510·60
12	374·00		

The elasticity of steam is employed as a moving power in the steam-engine. The construction of this machine depends on two properties of steam, namely, the expansive force communicated to it by heat, and its ready conversion into water by cold. The effect of both these properties is well shown by a little instrument devised by Wollaston. It consists of a cylindrical glass tube, six inches long, nearly an inch wide, and blown out into a spherical enlargement at one end. A piston is accurately fitted to the cylinder, so as to move up and down the tube with freedom. When the piston is at the bottom of the tube, it is forced up by causing a portion of water, previously placed in the ball, to boil by means of a spirit-lamp. On dipping the ball into cold water, the steam which occupies the cylinder is suddenly condensed and the piston forced down by the pressure of the air above it. By the alternate application of heat and cold, the same movements are reproduced, and may be repeated for any length of time. The moving power of

the steam-engine is the same as in this apparatus. The only essential difference between them is in the mode of condensing the steam. In the steam-engine, the steam is condensed in a separate vessel, called the *condenser*, where there is a regular supply of cold water for the purpose. By this contrivance, which constitutes the great improvement of Watt, the temperature of the cylinder never falls below 212° .

The formation of vapour is attended, like liquefaction, with loss of sensible heat. This is proved by the well-known fact that the temperature of steam is precisely the same as that of the boiling water from which it rises; so that all the heat which enters into the liquid is solely employed in converting a portion of it into vapour, without affecting the temperature of either, provided the latter is permitted to escape with freedom. The heat, which then becomes latent, to use the language of Black, is again set free when the vapour is condensed into water. The exact quantity of heat rendered insensible by vaporization may therefore be ascertained by condensing the vapour in cold water, and observing the rise of temperature which ensues. From the experiments of Black and Watt, conducted on this principle, steam of 212° , in being condensed into water of 212° , gives out as much heat as would raise the temperature of an equal weight of water by 950 degrees, all of which had previously existed in the vapour without being sensible to a thermometer.

The latent heat of steam and several other vapours has been examined by Dr. Ure, whose results are contained in the following table. (Phil. Trans. for 1818.)

	Latent heat.
Vapour of water at its boiling point	967°
Alcohol	442
Ether	302·379
Petroleum	177·87
Oil of turpentine	177·87
Nitric acid	531·99
Liquid ammonia	837·28
Vinegar	875

The disappearance of heat that accompanies vaporization was explained by Black and Irvine, in the way already mentioned under the head of liquefaction; and as the objections to the views of Irvine were then stated, it is unnecessary to mention them on the present occasion.

The variation of volume and elasticity in vapours is attended, as in gases, with a change of sp. heat and a consequent variation of temperature (page 54). Thus when steam, highly heated and compressed in a strong boiler, is permitted to escape by a large aperture, the sudden expansion is attended with a great loss of sensible heat: its temperature instantly sinks so much, that the hand may be held in the current of vapour without inconvenience. The same principle accounts for the fact, first ascertained by Watt, that distillation at a low temperature is not attended with any saving of fuel. For when water boils at a low temperature in a vacuum, the vapour is in a highly expanded state, and contains more insensible heat than steam of greater density. From some experiments by Sharpe in the Manchester Memoirs, and also by Clement and Desormes, (Thenard's Chemistry, i. 79, 5th Ed.) it appears that the sum of the sensible and insensible heat contained in equal weights of steam is exactly the same at all temperatures. Thus, steam at 212° , when condensed and reduced to 32° , gives out 950 degrees of insensible and 180 of sensible heat, the sum of which is 1130. The same weight of steam at 250° , on being condensed and cooled to 32° , gives out likewise 1130 degrees, of which 218 are sensible and 912 insensible heat; whereas at 100° its sensible heat is only 68°, and insensible 1062, forming the constant sum of 1130. The same is found by Despretz to be true of various other vapours, such as that of alcohol, ether, and turpentine.

EVAPORATION.

Evaporation as well as ebullition consists in the formation of vapour, and the only assignable difference between them is, that the one takes place quietly, the other with the appearance of boiling. Evaporation occurs at common temperatures. This fact may be proved by exposing water in a shallow vessel to the air for a few days, when it will gradually diminish, and at last disappear entirely. Most fluids, if not all of them, are susceptible of this gradual dissipation; and it may also be observed in some solids, as for example in camphor. Evaporation is much more rapid in some fluids than in others, and it is always found that those liquids the boiling point of which is lowest evaporate with the greatest rapidity. Thus alcohol, which boils at a lower temperature than water, evaporates also more freely; and ether, whose point of ebullition is yet lower than that of alcohol, evaporates with still greater rapidity.

The chief circumstances that influence the process of evaporation are extent of surface, and the state of the air as to temperature, dryness, stillness, and density.

1. Extent of surface. Evaporation proceeds only from the surface of fluids, and therefore, *ceteris paribus*, must depend upon the extent of surface exposed.

2. Temperature. The effect of heat in promoting evaporation may easily be shown by putting an equal quantity of water into two saucers, one of which is placed in a warm, the other in a cold situation. The former will be quite dry before the latter has suffered appreciable diminution.

3. State of the air as to dryness or moisture. When water is covered by a stratum of dry air, the evaporation is rapid even when its temperature is low. Thus in dry cold days in winter, the evaporation is exceedingly rapid; whereas it goes on very tardily, if the atmosphere contain much vapour, even though the air be very warm.

4. Evaporation is far slower in still air than in a current, and for an obvious reason. The air immediately in contact with the water soon becomes moist, and thus a check is put to evaporation. But if the air be removed from the surface of the water as soon as it has become charged with vapour, and its place supplied with fresh dry air, then the evaporation continues without interruption.

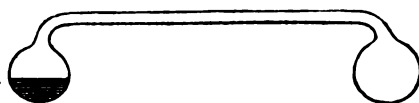
5. Pressure on the surface of liquids has a remarkable influence over evaporation. This is easily proved by placing ether in the vacuum of an air-pump, when vapour rises so abundantly as to produce ebullition.

As a large quantity of heat passes from a sensible to an insensible state during the formation of vapour, it follows that cold should be generated by evaporation. The fact may readily be proved by letting a few drops of ether evaporate from the hand, when a strong sensation of cold will be excited; or if the bulb of a thermometer, covered with lint, be moistened with ether, the production of cold will be marked by the descent of the mercury. But to appreciate the degree of cold which may be produced by evaporation, it is necessary to render it very rapid and abundant by artificial processes; and the best means of doing so, is by removing pressure from the surface of volatile liquids. Water placed under the exhausted receiver of an air-pump evaporates with great rapidity, and so much cold is generated as would freeze the water, did the vapour continue to rise for some time with the same velocity.

But the vapour itself soon fills the vacuum, and retards the evaporation by pressing upon the surface of the water. This difficulty may be avoided by putting under the receiver a substance, such as sulphuric acid, which has the property of absorbing watery vapour, and consequently of removing it as quickly as it is formed. Such is the principle of Leslie's method for freezing water by its own evaporation.*

The action of the cryophorus, an ingenious contrivance of the late Dr. Wollaston, depends on the same principle. It consists of two glass balls, perfectly free from air, and joined together by a tube as here represented.—

One of the balls contains a portion of distilled water, while the other parts of the in-



strument, which appear empty, are full of aqueous vapour, which checks the evaporation from the water by the pressure it exerts upon its surface. But when the empty ball is plunged into a freezing mixture, all the vapour within it is condensed; evaporation commences from the surface of the water in the other ball, and it is frozen in two or three minutes by the cold thus produced.

Liquids which evaporate more rapidly than water, cause a still greater reduction of temperature. The cold produced by the evaporation of ether in the vacuum of the air-pump is so intense as, under favourable circumstances, to freeze mercury.†

Scientific men have differed concerning the cause of evaporation. It was once supposed to be owing to chemical attraction between the air and water, and the idea is at first view plausible, since a certain degree of affinity does to all appearance exist between them. But it is nevertheless impossible to attribute the effect to this cause. For evaporation takes place equally *in vacuo* as in the air; nay, it is an established fact, that the atmosphere positively retards the process, and that one of the best means of accelerating it, is by removing the air altogether. The experiments of Dalton prove that heat is the true and only cause of the formation of vapour. He finds that the actual quantity of vapour which can exist in any given space is dependent solely upon the temperature. If, for instance, a little water be put into a dry glass flask, a quantity of vapour will be formed proportionate to the temperature.

* See art. Cold, in the Supplement to the Encyclopædia Britannica.

† See a paper by the late Dr. Marcet, in Nicholson's Journal, vol. xxxiv.

If a thermometer placed in it stands at 32° , the flask will contain a very small quantity of vapour. At 40° , more vapour will exist in it; at 50° , it will contain still more; and at 60° , the quantity will be still further augmented. If, when the thermometer is at 60° , the temperature of the flask be suddenly reduced to 40° , then a certain portion of vapour will be converted into water; the quantity which retains the elastic form being precisely the same as when the temperature was originally at 40° . It matters not, with regard to these changes, whether the flask is full of air, or altogether empty; for in either case, it will eventually contain the same quantity of vapour, when the thermometer is at the same height. The only effect of a difference in this respect, is in the rapidity of evaporation. The flask, if previously empty, acquires its full complement of vapour, or, in common language, becomes saturated with it, in an instant; whereas the presence of air affords a mechanical impediment to its passage from one part of the flask to another, and therefore an appreciable time elapses before the whole space is saturated.

Dalton found that the tension or elasticity of vapour is always the same, however much the pressure may vary, so long as the temperature remains constant, and there is liquid enough present to preserve the state of saturation proper to the temperature. If, for example, in a flaccid bladder containing a little water, the pressure on its surface be diminished, the vapour in the interior will expand proportionally; and consequently for the moment will diminish in elasticity, because the tension of gaseous substances at a constant temperature diminishes in the same ratio as the volume increases;—or, in other words, the elasticity varies inversely as the volume; but the vapour in the bladder will speedily recover its original tension, since the water will yield an additional quantity of vapour proportional to the increase of space. Again, if the pressure on the bladder be increased so as to diminish its capacity, the temperature remaining constant, the tension of the confined vapour will still continue unchanged, because a portion of it will be condensed proportional to the diminution of space; so that, in fact, the remaining space contains the very same quantity of vapour as it did originally. The same law holds good, whether the vapour is pure, or mixed with air or any other gas. The elasticity of watery vapour at temperatures below 212° was carefully examined by Dalton (Manchester Memoirs, vol. vi.); and

his results, together with those since published by Ure (Phil. Trans. 1818), are presented in a tabular form at the end of the volume. They were obtained by introducing a portion of water into the vacuum of a common barometer, and estimating the tension of its vapour by the extent to which it depressed the column of mercury at different temperatures.

A knowledge of the influence of heat and pressure over the volume of gaseous matter is elegantly employed in calculating the sp. gr. of vapour; but before giving the mode of making the calculation, it will be useful to explain what is meant by *specific gravity* or *density*. These terms are generally used to denote the compactness of a substance, or the quantity of ponderable matter contained in a body compared with the space which it occupies. The sp. gr. of a substance is found by dividing its weight by its volume. Thus, if d, w, v , represent the sp. gr., weight and volume of aqueous vapour, and d', w', v' , the sp. gr., weight and volume of air, then $d = \frac{w}{v}$, and $d' = \frac{w'}{v'}$. Hence, comparing these sp.

gravities, $d : d' :: \frac{w}{v} : \frac{w'}{v'}$; if the volumes are equal, then $d : d' :: w : w'$; and if the weights are equal, $d : d' :: \frac{1}{v} : \frac{1}{v'}$. Consequently, the sp. gravities of substances which have an equal volume, are directly as their weights; and when the weights are equal, the sp. gravities are inversely as the volumes. Accordingly, if we weigh an equal volume of any number of substances, temperature and pressure being the same in all, the sp. gr. of each respectively will be represented by its weight. Thus, Gay-Lussac ascertained that if a certain volume of air at 212° and 30 Bar. weigh 1000 grains; an equal volume of aqueous vapour, at the same temperature and pressure, will weigh 625 grains; and, therefore, the sp. gr. of steam is 625 compared to that of air as 1000. Atmospheric air is universally taken as a term of comparison for the sp. gr. of gaseous substances, and pure water for that of liquids and solids.

As gases expand and contract, from varying temperature and pressure, according to the same laws, it follows that the sp. gravities found at any one temperature and pressure are constant for all others. Thus if air is twice as heavy as an equal volume of a certain gas, both being weighed at 32° and 30 Bar., the same ratio will be found at 32° and 15 Bar., and at 212° and 30 Bar. The

same remark applies to vapours, except when they suffer condensation from diminution of temperature. For example, the density of air and steam, both being weighed at 212° and 30 Bar., is expressed by 1000 and 625: the same ratio is preserved at 212° and at any other pressure less than 30 Bar., because in that case the vapour will expand like air; but if the temperature be diminished, condensation occurs, and the density of the vapour falls below 625; or if the pressure be increased, the sp. gr. of the air increases, as the same quantity is forced to occupy less space, while that of the vapour is unaltered, the diminution of space being accompanied by a proportional condensation. Hence it happens that the sp. gravities of vapours vary with the temperature, as is exemplified by the following table, showing the greatest sp. gr. of aqueous vapour at the temperatures stated, the corresponding elasticities agreeably to Dalton's table, and the weight of 100 cubic inches of the vapour.

Temp.	Elasticity in inches of mercury.	Sp. gr.	Weight of 100 Cubic Inches.
32°	0.2	5.7292	0.13716 grains.
50°	0.375	10.3539	0.2478
60°	0.524	14.18306	0.3394
100°	1.860	46.6697	1.117
150°	7.42	170.61	4.084
212°	30	625	14.96

In calculating these sp. gravities it is assumed that the laws of gaseous expansion by varying heat and pressure are true,—that the sp. gr. of steam at 212° and 30 Bar. is 625, compared to air at the same temperature and pressure as 1000,—and that 100 cubic inches of air at 212° and 30 Bar. weigh 23.94 grains. The formula for the calculation is thus deduced:—If d is the sp. gr. of aqueous vapour at any pressure p , then since both the sp. gr. and elasticity of gaseous substances vary inversely as their volume, the sp. gr. and elasticity are proportional to each other; so that $d : 625 :: p : 30$,

and hence $d = 625 \cdot \frac{p}{30}$. This gives the sp. gr. of aqueous vapour at 212° and with an elasticity equal to p . In this state the vapour is rarefied, and will admit of being cooled down to a certain point, but not lower, say to t degrees above 32° , without condensation; and when it has reached that point, its sp. gr. has acquired a *maximum*. Its elasticity remains unchanged, because the loss of tension due to loss of heat is compensated for by diminution of volume. Its sp. gr. has increased exactly in the same ratio as its

volume has diminished, and therefore the formula of page 35 inverted will give the increased sp. gr. owing to decrease of temperature.

Hence we shall have $d = 625 \cdot \frac{p \cdot 480 + 180}{30 \cdot 480 + t}$. For ex-

ample, if we wish to calculate the greatest sp. gr. of aqueous vapour at 100° F., then $t = 68$, and the elasticity of that vapour by Dalton's table is 1.86. Inserting these values of t and p in the preced-

ing formula, we shall find $d = 625 \cdot \frac{1.86 \cdot 660}{30 \cdot 548} = 46.6697$.

It admits of inquiry whether liquids of weak volatility, such as mercury and oil of vitriol, give off any vapour at common temperatures. An opinion has prevailed, that evaporation not only takes place from the surface of these and similar liquids at all times, but that vapour of exceedingly weak tension is emitted at common temperatures from all substances however fixed in the fire, even from the earths and metals, when they are either in a vacuum, or surrounded by gaseous matter. It has accordingly been supposed, that the atmosphere contains diffused through it minute quantities of the vapours of all the bodies with which it is in contact; and this idea has been made the basis of a theory of the origin of meteorites. But this doctrine has been successfully combated by Faraday, in his essay On the Existence of a Limit to Vaporization (Phil. Trans. 1826). The argument employed by him is founded on the principle by which Wollaston accounted for the limited extent of the atmosphere. Since the volume of gaseous substances depends on the pressure to which they are subject, the air in the higher regions of the atmosphere must be much more rare than that in the lower, because the former sustains the pressure of a shorter atmospheric column than the latter; so that in ascending upwards from the earth, each successive stratum of air, being less compressed than the foregoing, is likewise more attenuated. Now it is found experimentally that the elasticity or tension of any gaseous matter diminishes in the same ratio as its volume increases; and, accordingly, whenever the tenuity of a portion of air, owing to its distance from the earth's surface or any other cause, is exceedingly great, its tension is exceedingly small. Reasoning on this principle, Wollaston conceived that at a certain altitude, probably at a distance of 40 or 50 miles from the surface of the earth, the rarefaction and consequent loss of elastic force is so extreme, that the

mere gravity of the particles becomes equal to their elasticity, and thus puts a limit to their separation.

What Wollaston suggested of aerial particles, Faraday supposes to occur in all substances; and this supposition is perfectly legitimate, because gaseous matter in general is subject to the same law of expansion, and is likewise under the influence of gravity. He infers that every kind of matter ceases to assume the elastic form, whenever the gravitation of its particles is stronger than the elasticity of its vapour. The loss of tension necessary for effecting this object may be accomplished in two ways, either by extreme dilatation, or by cold. For substances of great volatility, such as air and most gases, the former condition is necessary; because the degree of cold which we can command at the earth's surface diminishes their tension in a degree quite insufficient to destroy their elasticity. But the volatility of numerous bodies is so small, that their vapour at common temperatures approximates in rarity to the air at the limits of the atmosphere, and a small degree of cold may suffice for rendering its elasticity a force inferior to its opponent, gravity. In that case, the vapour would be entirely condensed. Faraday found that mercury, at a temperature varying from 60° to 80° , yields a small quantity of vapour; but in winter no trace of vapour could be detected. Hence it is inferred, that at the former temperature the elasticity of mercurial vapour is slightly superior to the gravity of its particles, and that in cold weather the latter power preponderates, and puts an entire check to the evaporation of mercury. The earths and metals which are more fixed than mercury have vapours of such feeble tension, that the highest natural temperature is unable to convert them into vapour. Another force, which co-operates with gravity in overcoming elasticity, is the attraction of aggregation, or the attraction exerted by a solid or liquid on the contiguous particles of the same substance in the gaseous form.—This argument affords very sufficient grounds for believing that the vapours of earthy and metallic substances are never present in the atmosphere; and Faraday has proved that several chemical agents, kept in a confined space with moisture during four years, did not undergo the slightest evaporation. (*Journal of the R. Inst. I. (N. S.)*)

The presence of vapour has a considerable influence over the bulk of gases; and as chemists often determine the quantity of gaseous substances by measure, it is important to estimate the in-

crease of volume due to the presence of moisture. The mode by which a vapour acts is obvious. When two gases, which do not act chemically on each other, are intermingled, each retains the elasticity suited to its volume, exactly as if the other gas were absent; so that the elasticity of the mixture is the sum of the elastic forces of its ingredients. The same remark applies to the mixture of gases and vapours. If a few drops of water are added to a portion of dry air, confined in a glass tube over mercury, the air will speedily become saturated with vapour, and must in consequence be increased in bulk. For the elastic power of the vapour being added to that previously exerted by the gas alone, the mixture will necessarily exert a stronger pressure upon the mercury that confines it, and will therefore occupy a greater space. It is equally clear that the degree of augmentation will depend on the temperature; for it is the temperature alone which determines the elasticity of the vapour.

As the elasticity of vapour is not at all affected by mere admixture with gases, it is easy to correct the fallacy to which its presence gives rise, by means of the data furnished by the experiments of Dalton. The formula for the correction is thus deduced. Let n be the bulk of dry air or other gas expressed in the degrees of a graduated tube; p the elasticity of the dry air, equal to the atmospheric pressure as measured by a barometer; n' the bulk of the air when saturated with watery vapour, and f the elasticity of that vapour (Biot's *Traité de Phys.* I. 303). Now, as the elasticity of a gas for equal temperatures is inversely as its volume, it follows that when the dry air increases in bulk from n to n' , its elasticity will diminish in the ratio of n' to n . Hence its elasticity ceases to be $= p$, and is expressed by $\frac{pn}{n'}$; p is then $= \frac{pn}{n'} + f$; that is, the elasticity of the moist air, added to the elasticity of the vapour present, is equal to the pressure of the atmosphere. From this last equation are deduced the following values: $pn + fn' = pn'$; $pn = pn' - fn'$; and $n = \frac{n'(p-f)}{p}$. One example will suffice for showing the use of this formula. Having 100 measures of air saturated with watery vapour at 60° , the barometer standing at 30 inches, how many measures would the air occupy if quite dry? $n' = 100$; $p = 30$; $f = 0.524$, the tension of watery vapour at 60° , according to Dalton's table. Hence

$n = \frac{100 \times (30 - 0.524)}{30} = \frac{100 \times 29.476}{30} = 98.25$, which is the answer required.

The preceding formula is true only when the gas is confined in a space which readily enlarges proportionally to the additional pressure, as when a tube full of air is inverted over mercury. If the gas is contained in a space which does not admit of enlargement, and a drop of water is admitted, the aqueous vapour adds its elastic force f to that of the gas p , causing the pressure against the containing vessel to be equal to $p + f$.

The presence of aqueous vapour in the atmosphere is owing to evaporation. All the accumulations of water upon the surface of the earth are subject by its means to a natural distillation; the impurities with which they are impregnated remain behind, while the pure vapour ascends into the air, gives rise to a multitude of meteorological phenomena, and after a time descends again upon the earth. As evaporation goes on to a certain extent even at low temperatures, it is probable that the atmosphere is never absolutely free from vapour.

The quantity of vapour present in the atmosphere is very variable, in consequence of the continual change of temperature to which the air is subject. But even when the temperature is the same, the quantity of vapour is still found to vary; for the air is not always in a state of saturation. At one time it is excessively dry, at another it is fully saturated; and at other times it varies between these extremes. This variable condition of the atmosphere as to saturation is ascertained by the hygrometer.

A great many hygrometers have been invented; but they may all be referred to three principles. The construction of the first kind of hygrometer is founded on the property possessed by some substances of expanding in a humid atmosphere, owing to a deposition of moisture within them; and of parting with it again to a dry air, and in consequence contracting. Almost all bodies have the power of attracting moisture from the air, though in different proportions. A piece of glass or metal weighs sensibly less when carefully dried, than after exposure to a moist atmosphere; though neither of them is dilated, because the water cannot penetrate into their interior. Dilatation from the absorption of moisture appears to depend on a deposition of it within the texture of a body, the particles of which are moderately soft and

yielding. The hygrometric property therefore belongs chiefly to organic substances, such as wood, the beard of corn, whalebone, hair, and animal membranes. Of these, none is better than the human hair, which not only elongates freely from imbibing moisture, but, by reason of its elasticity, recovers its original length on drying. The hygrometer of Saussure is made with this material.

The second kind of hygrometer points out the opposite states of dryness and moisture by the rapidity of evaporation. Water does not evaporate at all when the atmosphere is completely saturated with moisture; and the freedom with which it goes on at other times, is in proportion to the dryness of the air. The hygrometric condition of the air may be determined, therefore, by observing the rapidity of evaporation. The most convenient method of doing this is by covering the bulb of a thermometer with a piece of silk or linen, moistening it with water, and exposing it to the air. The descent of the mercury, or the cold produced, will correspond to the quantity of vapour formed in a given time. Leslie's hygrometer is of this kind.

The third kind of hygrometer is on a principle entirely different from the foregoing. When the air is saturated with vapour, and any colder body is brought into contact with it, deposition of moisture immediately takes place on its surface. This is often seen when a glass of cold spring water is carried into a warm room in summer; and the phenomenon is witnessed during the formation of dew, the moisture appearing on those substances only which are colder than the air. The degree indicated by the thermometer when dew begins to be deposited, is called the *dew-point*. If the saturation be complete, the least diminution of temperature is attended with the formation of dew; but if the air is dry, a body must be several degrees colder before moisture is deposited on its surface; and indeed the drier the atmosphere, the greater will be the difference between its temperature and the dew-point. Attempts were made to estimate the hygrometric state of the air on this principle by the Florentine Academicians, but the first accurate method was introduced by Le Roi, and since adopted by Dalton. It consists simply in putting cold water into a glass vessel, the outside of which is carefully dried, and marking the temperature of the liquid at which dew begins to be deposited on the glass. The water when necessary is cooled either by means of

ice or a freezing mixture. A convenient form of apparatus is a small cup made of thin silver, nicely gilt on the outside, capable of holding about half an ounce of water, and fitted into a case of turned wood lined with cloth, which serves as a stand for the cup during an observation. The water is cooled by successively adding a few grains of a powder made of equal parts of nitre and sal-ammoniac intimately mixed, stirring with the bulb of a small thermometer. As soon as dew is deposited, the temperature is noted; and the first observation is corrected by waiting until the cup and its contents grow warmer, and observing the temperature at which the dew begins to disappear. The last observation is the most trustworthy. This method, when deliberately performed, so that the cup, the solution, and the thermometer should have time to acquire the same temperature, is susceptible of great precision.

The hygrometer of Daniell, described in his *Meteorological Essays*, acts on the same principle. It consists of a cryophorus, as described at page 71, but modified somewhat in form, and containing ether instead of water. Within one of its balls is fixed a delicate thermometer, the bulb of which is partially immersed in the ether so as to indicate its temperature, and the other ball is covered with muslin. When the instrument is used, the muslin is moistened with ether, and the cold produced by its evaporation condenses the vapour within the cryophorus, and causes the ether to evaporate rapidly in the other ball. The cold thus generated chills the ether itself and the ball containing it; and in a short time its temperature descends so low, that dew is deposited on the surface of the glass. As soon as this takes place, the temperature is observed by the thermometer.

The same object is attained in a still easier way by means of a contrivance described by Jones of London (*Phil. Trans.* 1826), and soon after by Coldstream of Leith (*Phil. Journ.* ix. 155). It consists of a delicate mercurial thermometer, the bulb of which is made of thin black glass, and, excepting about a fourth of its surface, is covered with muslin. On moistening the muslin with ether, the temperature of the bulb and mercury falls, and the uncovered portion of the bulb is soon rendered dim by the deposition of moisture. The temperature indicated at that instant by the thermometer is the dew-point. It appears from some remarks by Daniell in the *Quarterly Journal of Science*, that this hygrometer was originally invented in Germany; so that Jones and Coldstream

are second inventors. Daniell considers the instrument inaccurate, believing that, as the ether is applied to a part only of the bulb, the mercury within will be cooled unequally; that the portion corresponding to the covered part of the bulb will be colder than the mercury opposite to the exposed part; and consequently that the dew-point will appear lower than it ought to be. This objection certainly applies when the muslin is rendered very moist with ether, and the temperature of the bulb is rapidly reduced; but when the cooling is slowly effected, I believe the indications of this hygrometer to be at least as correct as those afforded by the very elegant, yet more costly and less portable, apparatus of Daniell. For facts confirmatory of this opinion the reader may consult an essay by Foggo, junior, of Leith. (*Brewster's Journal* vii. 36.)

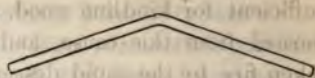
It is desirable on some occasions, not merely to know the hygrometric condition of air or gases, but also to deprive them entirely of their vapour. This may be done to a great extent by exposing them to intense cold; but the method now generally preferred is by bringing the moist gas in contact with some substance which has a powerful chemical attraction for water. Of these none is preferable to chloride of calcium.

CONSTITUTION OF GASES WITH RESPECT TO HEAT.

From the experiments of Faraday on the liquefaction of gaseous substances, gases may be viewed as the vapours of extremely volatile liquids. Most of these liquids, however, are so volatile, that their boiling point, under the atmospheric pressure, is lower than any natural temperature; and hence they are always found in the gaseous state. By subjecting them to great pressure, their elasticity is so far counteracted that they become liquid. But even when thus compressed, a very moderate heat is sufficient to make them boil; and on the removal of pressure they resume the elastic form, most of them with such violence as to cause a report like an explosion, and others with the appearance of brisk ebullition. Intense cold is produced at the same time, in consequence of their heat passing from a sensible to an insensible state.

The process for condensing gases (*Philos. Trans.* 1823) consists in exposing them to the pressure of their own atmospheres. The materials for producing the gas are put into a strong glass tube, which is afterwards sealed hermetically, and bent in the middle, as

represented by the figure. The gas is generated, if necessary, by the application of heat; and when the pressure becomes sufficiently great, the liquid is formed and collects in the free end of the tube, which is kept cool to facilitate the condensation. Most of these experiments are attended with danger from the bursting of the tubes, against which the operator must protect himself by the use of a mask.



The pressure required to liquefy gases is very variable, as will appear from the following table of the results obtained by Faraday.

Sulphurous acid gas	2	atmospheres at	45°
Sulphureted hydrogen gas	17		50°
Carbonic acid gas	36		32°
Chlorine gas	4		60°
Nitrous oxide gas	50		45°
Cyanogen gas	3.6		45°
Ammoniacal gas	6.5		50°
Muriatic acid gas	40		50°

Additional light has been thrown on the nature of gases by M. Thilorier, who has succeeded in obtaining carbonic acid gas in a solid state (*Ann. de Ch. et Ph.* lx. 431). It is procured by directing a jet of the liquid carbonic acid into a small glass phial, which is rapidly filled with solid carbonic acid in the form of a white flocculent powder. The solidification is evidently produced by the cold occasioned by the sudden transition of a liquid into a gas, in which state it occupies a space 400 times greater than its original volume. The degree of cold thus produced is estimated by Thilorier at -148° , at which temperature carbonic acid appears to be entirely deprived of its elastic force; for the solid exposed to the ordinary atmospheric pressure and temperature evaporates slowly and quietly, and is gradually converted into carbonic acid gas.

SOURCES OF HEAT.

The sources of heat may be reduced to six:—1. The sun. 2. Combustion. 3. Electricity. 4. The bodies of animals during life. 5. Chemical action. 6. Mechanical action.—All these means of procuring a supply of heat, except the last, will be more conveniently considered in other parts of the work.

The mechanical method of exciting heat is by friction and percussion. When parts of heavy machinery rub against one another, the heat excited, if the parts of contact are not well greased, is

sufficient for kindling wood. The axle-tree of carriages has been burned from this cause, and the sides of ships are said to have taken fire by the rapid descent of the cable. Count Rumford has given an interesting account of the heat excited in boring cannon, which was so abundant as to heat a considerable quantity of water to its boiling point. It appeared from his experiments that a body never ceases to give out heat by friction, however long the operation may be continued; and he inferred from this observation that heat cannot be a material substance, but is merely a property of matter. Pictet observed that solids alone produce heat by friction, no elevation of temperature taking place from the mere agitation of fluids with one another. He found that the heat excited by friction is not in proportion to the hardness and elasticity of the bodies employed. On the contrary, a piece of brass rubbed with a piece of cedar wood produced more heat than when rubbed with another piece of metal; and the heat was still greater when two pieces of wood were employed.

SECTION II.

LIGHT.

OPTICS, from *ὀπτική* *I see*, is the science which treats of light and vision. On the nature of light two rival theories exist, the *undulatory* and *corpuscular*. Prior to and about the time of Newton's celebrated analysis of solar light in 1672, Descartes, Hooke, Huygens, and others had entertained the former; but Newton, in adopting the latter, led to its almost general reception. He considered light to consist of inconceivably minute particles, too subtle to exhibit the common properties of matter, though really material, which emanate from luminous bodies, such as the sun, the fixed stars, and incandescent substances, travel with immense velocity, and excite the sensation of light by passing bodily through the substance of the eye, and striking against the expanded nerve of vision, the retina. This theory, with which the language of optics has become identified, prevailed with almost no opposition from the time of Newton till 1801, when the undulatory theory was revived and supported with great ability by Young (Phil. Trans.). By the researches of others, the testimony in favour of this doctrine gradually gained ground, and at present it is all but generally

adopted. While some phenomena, as the absorption and refraction of light, are even yet obscurely explained by either theory, others, especially the phenomena of interference and polarized light, are wholly inexplicable by the corpuscular, and receive a most lucid explanation by the undulatory theory. On this ground the former is considered untenable, and the latter alone suitable to the present condition of science. But to enter at length into this argument would be so foreign to the design of this treatise, that the shortest possible notice must suffice, the reader being referred for more full information to Pouillet's *Elémens de Physique*, Young's *Essays*, Airy's *Tracts*, 2nd edition, and Herschel's article on Light in the *Encyclopedia Metropolitana*.

It is assumed, as the basis of the undulatory theory, that a subtile ether, eminently rare and elastic, pervades the whole universe, being present in the heavenly spheres, in the atmosphere, and within the pores of the densest bodies in nature. The sun and other luminous bodies, owing to peculiar vibratory movements within their substance, throw the contiguous ether within or about them into corresponding vibrations, which are thence conveyed along from one particle of ether to another, and excite the sensation of light by impelling the retina, just as hearing is caused by impulses on the auditory nerve by analogous vibrations of the air or some other elastic medium. There is thus set up between light and sound an analogy which in numerous respects is most intimate and instructive. In the travelling of light or sound the individual particles of ether or air have a very limited range of motion; the office of each particle is to impart to its neighbour the impulse which it has itself received, and it is this impulse which travels; just as when standing-corn is agitated by the wind, or a stone is thrown into a pond, waves extend rapidly over the field or along the water, though the movement of each ear of corn or particle of water is very limited.—When a tuning fork or a tense cord is set into vibration, they move to and fro, as do all vibrating bodies; each forward motion gives a separate blow to the air, and impulse after impulse passes through the aerial strata with a velocity of succession depending on the velocity with which the vibrations of the fork or cord succeed each other. If these impulses recur at intervals not less than about sixteen times in a second, a continuous sound is heard, the sensation from one impulse continuing till another succeeds. When the impulses are sufficiently frequent and at

equal intervals, a musical note is heard, the pitch of which depends on the frequency of recurrence, the note being more and more acute as the recurrences are more rapid. Light and colours are ascribed to a similar cause. The ethereal impulses do not excite the sensation of light unless they recur with a certain frequency; and on that frequency, which, as in ærial impulses, may vary, depend the various colours. The violet is due to the most frequently recurring impulses, corresponding to acute tones, the red to the least frequent, and the other tints of the spectrum to impulses of intermediate frequency. When a number of ethereal impulses of different frequency impel the same point of the retina at the same instant, the sensation of white light is produced.—From the analogy between the succession of impulses in air or ether to that of waves in water, the term *wave* is applied to the former cases. One entire wave in water is the distance between the highest part of one wave and the highest part of the following one, that distance being the *length of the wave*: that length is variable, increasing as the time increases with which wave follows wave. So, a wave in air is the distance between two successive impulses, and its length increases as the time between the recurrence of the impulses: the more acute the tone, the shorter the ærial wave which causes it. The same distinctions apply to ethereal waves; and hence, in the prismatic colours, the waves causing red light are the longest, and those of violet the shortest.—In the vibration of a cord, each forward movement gives a forward impulse to the air: in the interval between two such impulses the cord moves backward, and leaves a space behind, which the air by its elasticity immediately occupies, causing a backward impulse. There is, thus, in a sounding column of air, a continued vibration, or motion to and fro, of the ærial particles, partaking of the character of the vibrations which set the air in motion. The same is believed to occur in ether. Now, should two forward ærial impulses fall simultaneously on the ear, each would co-operate with the other, and the resulting sound be strengthened: but if two equal and opposite impulses coincide, each destroys the effect of the other, and total silence results. The impulses *interfere* with each other. Phenomena of this kind are well known in regard to sound, and were the undulatory theory true, something similar should be met with in optics: two equal ethereal impulses should double the light if they acted together in the same direction, and should produce total darkness when their directions were op-

posed. This is actually found to occur, and constitutes what is termed *interference*—a phenomenon wholly irreconcilable with the corpuscular theory.

Having thus given a general notion of the undulatory theory, I proceed to state the laws of light in ordinary language. By *light* is understood the ethereal impulses which cause the sensation of light: when light is spoken of as emanating from a point, it is meant that the ethereal impulses so emanate; when light is said to be reflected, it is understood that the ethereal impulses rebound, in the same manner as aërial impulses rebound in forming an echo.

Diffusion of Light.—Light emanates from every visible point of a luminous object, and is equally distributed on all sides if not intercepted, diverging like radii drawn from the centre to the circumference of a circle. Thus, if a single luminous point were placed in the centre of a hollow sphere, every point of its concavity would be illuminated, and equal areas would receive equal quantities of light. The smallest portion of light which can be separated from contiguous portions is called a *ray of light*. Each ray, when not interrupted in its course, and while it remains in the same medium, moves in a straight line; as is obvious by the appearance of shadows cast by the side of a house, or of a sunbeam admitted through a small aperture into a dark room. Owing to these modes of distribution, it follows that the quantity of light which falls upon a given surface decreases as the square of its distance from the luminous object increases, the same law which regulates the heating power of a hot body. (Page 15.)

The passage of light is progressive, time being required for its motion from one place to another. By astronomical observations it is found that light travels at the rate of nearly 195,000 miles in a second of time, and would require about eight minutes to pass from the sun to the earth. Owing to this prodigious velocity, the light caused by the firing of a cannon or a sky-rocket is seen by different spectators at the same instant, whatever may be their respective distances from the rocket, the time required for light to travel 100 or 1000 miles being inappreciable to our senses.

When light falls upon any body, it may, like radiant heat (page 15), dispose of itself in three different ways, being *reflected*, *refracted*, or *absorbed*. The phenomena connected with the two former modes of distribution I shall proceed to consider in succes-

sion ; while those of absorbed light will be included under the head of *Decomposition of Light*.

REFLECTION OF LIGHT.

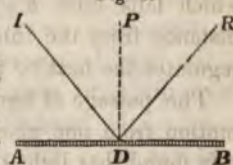
Light may be reflected by all media, whether solid, liquid, or gaseous, when it passes from one medium into another of a different nature or density ; but there is great difference in the power of reflection. Bright metallic surfaces, such as polished brass and silver, or clean mercury, reflect nearly all the rays which fall upon them ; while those which are dull and rough reflect but few. The reflection of light, like that of heat, takes place at the surface of bodies, and appears influenced rather by the condition of the surface than by the nature of the reflecting body. The direction of the reflected ray, whatever may be the nature or figure of the reflecting surface, is regulated by these two laws.

I. The incident and reflected rays always lie in the same plane, which plane is perpendicular to the reflecting surface.

II. The incident and reflected rays always form equal angles with the reflecting surface ; or, what amounts to the same, the angle of incidence is always equal to the angle of reflection.

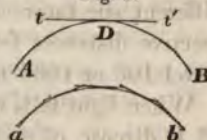
Let AB , figure 1, represent a plane mirror, ID the direction of a ray falling on AB at the point D , and DP a line perpendicular to the mirror AB . Then a plane passing through IDP will be perpendicular to AB , and, by the first law, the reflected ray DR will lie *somewhere* in that plane. Also, by the second law, the angle of reflection RDP must be equal to the angle of incidence IDP . Hence, as soon as the direction of the incident ray is given, that of the reflected ray is known also.

Fig. 1.



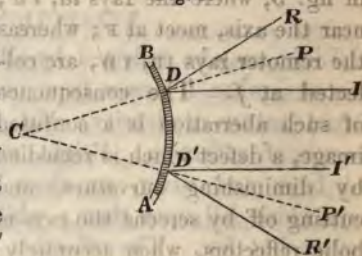
These laws apply equally to convex and concave mirrors. A circle or any curve may be viewed as a polygon with very short sides circumscribing the curve, as shown in ab , fig. 2 ; and on this principle a tangent tt' at any point D of a curve AB may be taken as identical at the touching point with the curve itself. Similarly, may a plane tangent to a curved surface be considered as part of that surface at the point of contact. The action of a curved mirror

Fig. 2.



may hence be referred to that of a number of tangent planes, which will reflect light agreeably to the two laws above mentioned. Thus, let AB , fig. 3, be a convex mirror, being a segment of a sphere, the centre of which is c ; let ID , ID' be parallel rays, incident at D , D' . The dotted lines DP , $D'P'$ will be respectively perpendicular to the tangent at D , D' ; the angles of incidence are IDP , $ID'P'$; and PDR , $P'D'R'$ the angles of reflection. Parallel rays falling on a convex mirror are obviously scattered or made to diverge.

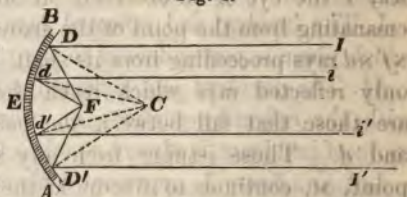
Fig. 3.



On the same principle must parallel rays falling on a concave spherical mirror, as represented by fig. 4, be so reflected as to converge and meet together

Fig. 4.

at one point F , which is called its *focus for parallel rays*, or its *principal focus*, and is situated midway between the centre c , and the axis of the mirror E . The dotted lines represent the perpendicular to the tangent at the respective points of incidence, D , D' , d , d' . From the same figure it is obvious that the diverging rays emitted by a light placed in the focus of a concave mirror are rendered parallel by reflection. If the light be placed between E and F , then the rays will continue divergent after reflection. On placing the light between F and c , the incident rays, diverging less rapidly than when the light was at F , will converge after reflection, and meet at some point beyond c , which point is more remote from c the nearer the light is to F . When the light is at c , all the rays are reflected back to c ; since each ray will then be perpendicular to the tangent at its point of incidence. The student will easily comprehend these statements if he will but take rule and compass, and draw a few figures for himself.



The statement above made, that parallel rays are collected into one point by reflection from a concave spherical mirror, is not strictly correct. When the mirror is very flat, being a small segment of a large sphere, the rays meet very nearly in one point; but they are far from doing so when the curvature of the mirror

is considerable. This defect of spherical mirrors, which arises from their form, and is termed *spherical aberration*, is exhibited in fig. 5, where the rays $id, i'd'$, near the axis, meet at F ; whereas the remoter rays $ID, I'D'$, are collected at f . The consequence of such aberration is a confused image, a defect which is remedied by diminishing curvature, and cutting off by screens the rays most distant from the axis. Parabolic reflectors, when accurately made, are entirely free from this inconvenience.

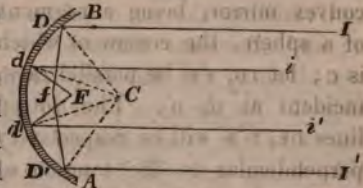


Fig. 5.

The position in which objects are seen after being reflected will now be easily understood. Let MN , fig. 6, be an arrow placed before a plane mirror AB , E the eye of an observer, Mc Me rays emanating from the point of the arrow, and Nf Nd rays proceeding from its shaft. The only reflected rays which reach the eye are those that fall between the points c and d . Those issuing from any single point, M , continue to diverge at the same rate after as before reflection; and, though they are reflected and enter the eye separately, they are collected together by the refracting power of that organ, and appear to the observer to issue from a point m , at which, if continued back, they would intersect. The same is true of rays issuing from N , and from all points intermediate between M and N . By inspecting the figure it will be seen that each part of the image mn is at the same distance behind the mirror as the object MN is before it, and that the image and object have the same length; consequences which flow necessarily from the laws of reflection and the known properties of triangles.

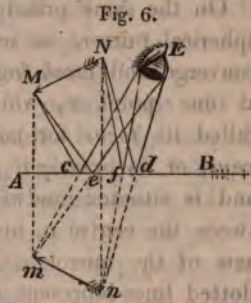
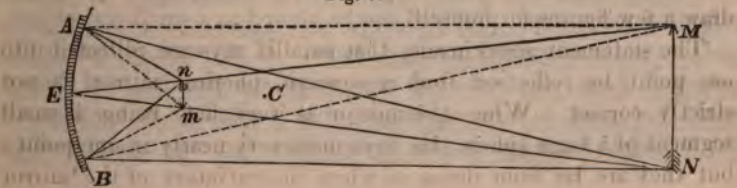


Fig. 6.

Again, let the arrow MN , fig. 7, represent a high distant object,

Fig. 7.



towards which a spherical mirror AB is directed. Rays emanating from M and falling on the mirror at A , E , and B , will be so reflected that they all meet at a point m ; rays diverging from N , and reaching the same points of the mirror, will be collected at n ; and all points intermediate between M and N will be represented along the line mn , forming a small inverted image of the object. As the rays prior to reflection were divergent, their focal points will be nearer the centre c than the focus for parallel rays. The image mn will be much smaller than the object, the ratio of their lengths being directly as their distances from the mirror; a relation which the geometric reader will discover for himself by inspecting the figure: If MN be 1000 feet from the mirror, and mn at one foot, the image will be diminished in length 1000 times. Hence, as the size and position of the image can be measured, the distance of the object may be calculated if we know its size; or its size may be inferred from a knowledge of its distance.

The construction of the simple reflecting telescope depends on the principle just explained. The small size of the image is compensated for, partly by its brightness, since each point is formed by the concentration of many rays, and partly by the advantage of placing the eye close to it. In order to see the image mn , the observer may place in the focus a piece of ground-glass or tissue-paper; or, a hole being cut in the mirror at E , the image may be received on a small plane mirror placed in the focus, and be reflected to the observer at E . Instead of using a plane mirror for this purpose, mn may be considered as a new *object*, and be reflected by a second smaller concave mirror placed between mn and c , and in front of AB ; for the converging rays which meet at any point m of the image cross each other at that point, and then diverge exactly as though the place of the image were occupied by a real arrow. The second mirror may be so placed as to magnify the image mn ; and the second image may be still further enlarged by a convex lens. Compound reflecting telescopes are constructed on this principle.

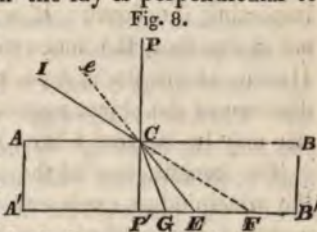
The arrangement displayed by figure 7 is exactly that of a simple reflecting microscope, provided mn be viewed as a small real object, and MN as its magnified inverted image. If mn were placed in the principal focus, the reflected rays would be parallel, and hence could not meet to form an image; but if situated rather beyond the principal focus, as in the figure, then the rays converge after

reflection, and give an enlarged image of the small object. The ratio of the length of the object and image will, as before, be as their respective distances from the mirror.

REFRACTION OF LIGHT.

Light traverses the same transparent medium, such as air, water, or glass, in a straight line, provided no reflection occurs, and there is no change of density; but when it passes from one medium into another, or from one part of the same medium into another of a different density, a change of direction always ensues at the plane of junction of the media, except when the ray is perpendicular to that plane. For instance, let $AB A'B'$,

fig. 8, represent a vertical section of a vessel full of water, and PP' the perpendicular to the surface of the water at the point c . Should a ray of light enter the water perpendicularly to its surface, as in the line of pc , it will continue on its course to p' without deviation; but if it descend obliquely, as in the direction of rc , it will suffer a bend at c , and proceed to E , instead of advancing along the dotted line to r . Conversely, were a ray of light to emanate from E and emerge at c , it would not advance to e , but take the direction of cr . By comparing the direction of the refracted ray in these two cases in relation to the vertical pp' , it will be seen that the ray approaches the perpendicular in entering from air into water, and recedes from it in passing out of water into air. The same remark applies to the passage of light from or into air into or out of solid or liquid media in general.



Bodies differ in their power of refracting light. In general, the denser a substance is, the greater is the deviation which it produces. If in fig. 8 sulphuric acid were mixed with the water, the ray rc would be refracted to some point between E and c ; and if a solid cake of glass were substituted for that liquid, the refracted ray would be bent down to cG . But this is far from universal:—alcohol, ether, and olive oil, which are lighter than water, have a higher refractive power. Observation has shown it to be a law, to which no exception is yet known, that oils and other highly inflammable bodies, such as hydrogen, diamond, phosphorus, sulphur, amber, olive oil, and camphor, have a refractive power which is

from two to seven times greater than that of incombustible substances of equal density. But whatever may be the refractive power of bodies in relation to each other, refraction is always governed by the two following laws, discovered in 1618 by Snell, though usually ascribed to Descartes.

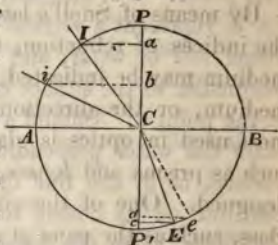
1. The direction of the incident and refracted ray is always in a plane perpendicular to the surface common to the media.

2. The sine of the angle of incidence and the sine of the angle of refraction are in a constant report for the same media.

The first law is similar to the first law of reflection already explained (page 87). To explain the second law, let $\triangle ABE$, fig. 9, be a vertical section of a refracting medium,

rr' the perpendicular to it, ic a ray of light incident at c , and ce the refracted ray. Then icr is the *angle of incidence*, and ecr' the *angle of refraction*. Also from c , as a centre, with any radius ci , and in the plane of the ray ice , draw a circle; and from the points i and e , where the course of the ray cuts the circle, let fall ia , ec at right angles to rr' . Then may ia be considered the *sine* of the angle of incidence, and ec the *sine* of the angle of refraction. The second law denotes that these lines are for each substance in a constant ratio, whatever may be the direction of the incident ray. In the figure, the sine of the angle of refraction is to the sine of the angle of incidence as 1 to 2; and this ratio being once determined, each ray must conform itself to it, so that any angle of incidence being given, the direction of the refracted ray may be foretold. Thus, if ic be a second ray incident at c , of which ib is the sine of the angle of incidence, the ray will be bent into such a course, that ed shall be to ib as 1 is to 2. This ratio is nearly that observed in glass made of one part of flint to three of oxide of lead. In common flint glass the ratio is nearly as 1 to 1.6; in water it is as 1 to 1.336; in oil of cassia as 1 to 1.641; in diamond as 1 to 2.755; in phosphorus as 1 to 2.224; and in melted sulphur as 1 to 2.148. By thus representing the sine of the angle of refraction by 1, the sines of the angle of incidence in all bodies refer to the same unit of comparison, and are therefore at once comparable with each other: such numbers are called *indices of refraction*, and indicate the degree of refractive

Fig. 9.



power. For example, the *index of refraction* for water is 1.336; for flint-glass 1.6; and for diamond 2.755.

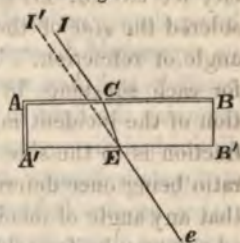
Subjoined is a table of the refractive indices of gases, that of a vacuum being unity.

Name of Gas.	Ref. Index.	Name of Gas.	Ref. Index.
Oxygen	1.000272	Carbonic Acid	1.000449
Hydrogen	1.000138	Hydrochloric Acid	1.000449
Nitrogen	1.000300	Ammonia	1.000385
Chlorine	1.000772	Cyanogen	1.000834
Protoxide of Nitrogen	1.000503	Hydrocyanic Acid	1.000451
Binoxide of Nitrogen	1.000303	Sulphurous Acid	1.000665
Olefiant Gas	1.000678	Hydrosulphuric Acid	1.000644
Marsh Gas	1.000443	Bisulphuret of Carbon	
Ether Vapour	1.001530	Vapour	1.001500
Carbonic Oxide	1.000340		

By means of Snell's laws of refraction, and with a knowledge of the indices of refraction, the course of a ray of light through any medium may be indicated, whatever be the nature or figure of that medium, or the direction of the ray. The refracting substance most used in optics is glass, which is ground into different forms, such as prisms and lenses, according to the purpose for which it is designed. One of the simplest cases is the refraction of a plane glass, such as the pane of a window.

Let ic , fig. 10, be a ray incident on the upper side, AB , of a plane glass, and CE the refracted ray: at its exit at the under side, $A'B'$, which is parallel to AB , it will be refracted to the same amount as at its entrance, and will pass on in the direction of Ee , appearing to an observer at e to have come along the line $I'E$, parallel to its real course ic . Hence, in looking at an object through a window, it is not seen in its real position; but as all the rays are similarly affected, the object is not distorted, provided the opposite sides of the glass are really parallel.

Fig. 10;



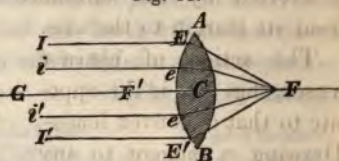
In studying the influence of curved media on light the same rule is to be observed as in reflection by curved mirrors (page 88): a plane tangent to the curved surface at each point of incidence is to be drawn or imagined, and the direction of the ray deduced in reference to that plane. On applying this rule to convex and concave lenses, it is found that the former act like concave mirrors, and tend to collect the refracted rays together; whereas a concave lens, like a convex mirror, tends to scatter them. Figure 11 represents

parallel rays falling upon a doubly convex lens, the two curved surfaces of which are shown by the vertical section AB . The ray GF , which falls perpendicularly, goes without deviation through the middle or *axis* of the lens. The other rays enter and quit the lens so as to form a smaller angle on one side than on the other, and the acute angle obviously lies on the side towards the axis; every ray is bent towards that axis by both surfaces; and as, from the figure of the lens, the rays most distant from the axis approach the lens at the smallest angle, they also suffer the greatest refraction. The result is, that the rays converge and meet at a point F , termed the *focus of parallel rays*, or the *principal focus*. Its distance from c varies both with the curvature of the lens and the refracting power of the glass with which it is made. With glass of the same quality the focal distance depends on the figure of the lens, the greatest convexity giving the shortest focal distance.

As the lens in figure 11 brings parallel rays into a focus at F , it is obvious that rays diverging from a luminous object placed at F will be rendered parallel by the same lens, the course of the rays being simply reversed. Were a light situated between F and c , its rays would diverge so much that the lens could not render them parallel, and they would continue divergent after refraction. On removing the light to the right of F , the incident rays have such diminished divergence that they converge after refraction, and meet at a certain distance to the left of the lens, which distance diminishes as the light recedes from F ; until at length, when the luminous object is so far on the right side of the lens that the incident rays may be considered parallel, they will be bent into a focus at F' .

Convex lenses are subject to the defect called *spherical aberration* equally with concave mirrors (page 89), and from the same cause. The spherical figure of a convex lens causes undue refraction of the rays incident near its margin, so that such rays have a shorter focal distance than those incident near its axis. The defect is more conspicuous in lenses of considerable curvature than in flat ones; and it may be remedied by intercepting the marginal rays with an opaque screen, or by forming such a combination of lenses as may augment the convergence of the rays near the axis without equally acting on those more distant from it. In the eye this evil

Fig. 11.



is averted by the substance of the lens increasing in density from its margin to the axis.

The action of concave lenses, fig. 12, is the opposite to that of convex lenses. Drawing a tangent to any point of the curve, and constructing the sines of incidence and refraction as in figure 9, it will be found that parallel rays will be so refracted by both surfaces of a doubly concave lens, that they will diverge as if they had emanated from a common point F before the lens, termed its principal focus, the position of which depends on the refracting power of the substance of the lens, as well as on its curvature. Conversely, the rays D', D, d, d' , converging towards the principal focus F of a doubly concave lens, will be rendered parallel by such lens: if their original convergence were less rapid, they would diverge after refraction; but if their convergence were to a point between F and c , they would still converge after refraction, and meet somewhere along the axis FC , at a point less remote the greater the original convergence. Rays already divergent will diverge still more after passing through a concave lens. Thus the influence of concave lenses, whether concave on both sides or on one only, is exactly opposed to that of convex lenses. The former tend to diminish or destroy convergence, and to render diverging rays still more divergent; whereas the latter diminish or destroy divergence, and give increased convergence to rays already convergent.

The refracting properties of convex lenses are extensively applied in the construction of *refracting* telescopes and microscopes, the object being, as in *reflecting* telescopes and microscopes, to obtain a distinct small image of a large distant object, or a magnified representation of a near small object. The nature of such combinations is illustrated by the annexed woodcut, fig. 13, in which ab is a doubly

Fig. 12.

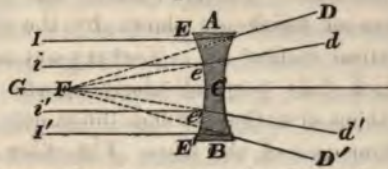
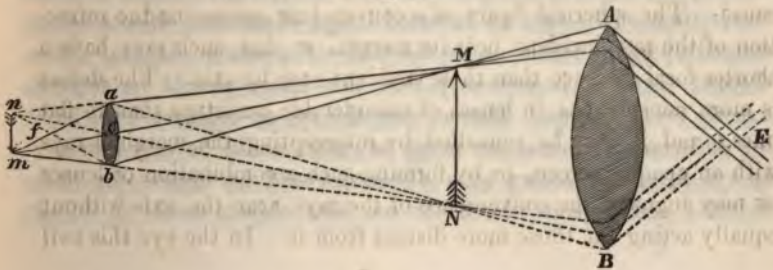


Fig. 13.



convex lens acting on rays from a distant object represented by the arrow MN . As the incident rays are not parallel, but divergent, the rays from each point of MN will be collected into a focus at a distance behind ab , somewhat greater than the focus of parallel rays f ; and an inverted image nm will be produced. The length of the image to that of the object will be directly as their respective distances from the centre of the lens ab , exactly as in the reflecting telescope (page 90). If MN is well illuminated, its image will be bright, since each point is formed by the confluence of many rays. The image will be inverted, the rays which emanate from the upper part of the object forming the lower part of the image, and conversely. The direction in which the rays from any point m meet, may be found by drawing a straight line from m through the centre c of the lens ab ; for as the ray mc enters the lens above the axis at the same distance as it quits it below the axis, the second refraction is exactly the reverse of the first, and the ray emerges as though it had passed through a *plane* glass (fig. 10),—moving onwards, not strictly in the same straight line, (though for convenience it is usually represented as such,) but in a line parallel to it. Figure 13 likewise exhibits the application of a convex lens in the construction of a microscope. For if nm be a small object placed a little beyond the principal focus of the lens ab , the rays will be so refracted as to form a large inverted image MN , the size of which is determined by the rule above mentioned.

A convex lens fitted into the wall of a darkened chamber constitutes the arrangement of a *camera obscura*, the inverted images of external objects being received on a disk of paper or a white board. In the simple telescope the lens is placed at the extremity of a tube of such length that the image may be formed within the tube, and the observer looks from the other end at the image formed in the air. The eye acts on the same principle. Luminous rays entering the transparent parts of the eye are refracted by the cornea and crystalline lens, and are brought into a focus at the bottom of the eye, an inverted image of external objects being formed upon the retina as on the table of a camera obscura. For distinct vision it is necessary that this image should be formed exactly on the retina. Hence, were the eye an ordinary lens, having an invariable focus, our range of vision would be very narrow: an eye fitted for seeing at a distance would be useless for near objects; and persons who could see near objects would be blind

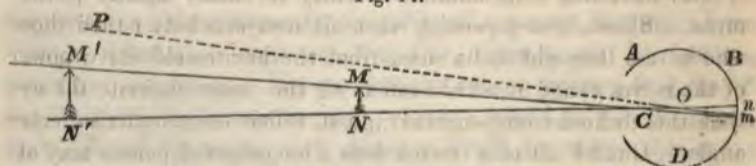
to remote ones. Two rays emanating from a distant point cannot *both* fall upon so small an object as the eye, unless they are nearly parallel; for if they diverged by even a very small angle, they would before reaching the eye separate by an interval exceeding the diameter of the cornea. On the contrary, rays in rapid divergence may enter the eye, provided the point from which they emanate be close to it; and the nearer the object, the more divergent the rays which enter. When, therefore, we observe a distant landscape, then successively notice nearer and nearer objects, and lastly cast the eyes upon the page of a book only six inches distant, we receive rays coming from a multitude of different objects, each set of rays having its own peculiar divergence, and requiring a separate focus; and yet, so wonderful is the adjusting power of the eye, a single minute suffices for distinctly seeing all the objects so beheld, without the consciousness of an effort.

The adjustment of the eye for different distances appears to depend on a power of increasing or decreasing the distance between the posterior part of the eye and the lens; though the mechanism by which this is accomplished is unknown. Some ascribe it to a change in the figure of the whole eye-ball, produced by the muscles which move the eye; but Brewster, I think with better reason, considers the position of the lens to be varied by the same contractile tissue which determines the movements of the iris and the size of the pupil. To this adjusting power, however, there is a limit. The distance at which most persons see small objects distinctly is about six inches: at shorter distances the rays are so divergent, that their focal point falls behind the retina, and indistinct vision is the consequence. Persons called *long-sighted* are unable to see near objects distinctly, owing to a weak refracting power of the eye, due to deficient convexity or density in the humours of the eye. This is the infirmity of advancing life, and is remedied by convex glasses, which cause diverging rays to be parallel or slightly convergent. In *short-sighted* persons the refractive power, either from undue convexity or undue density of the cornea and lens, is so powerful, that all rays which do not diverge rapidly are brought to a focus before they reach the retina. Youth is the period most obnoxious to this imperfection, and assistance is derived from a concave glass, which causes parallel rays to diverge, and thereby counteracts the refracting influence of the eye.

Objects are seen aright though their images on the retina are inverted. The direction in which each point of an object is seen may depend either on the direction of the rays which form it, or on the part of the retina which is impressed. On inspecting the image nm , figure 13, it will be seen that any point n is formed by a multitude of rays lying within the angle bna , each of which has a different direction from the others; and yet when a similar collection of rays is formed on the retina, the observer sees only one point N , situated nearly in the direction of ncn . Such and similar considerations justify the belief, that the direction in which a luminous point is seen depends not on the direction of the rays as they enter the eye, but on the part of the retina which is impressed. Brewster contends that the line of visible direction is always perpendicular to that part on which a ray falls; and that, as the eye-ball is nearly a perfect sphere, these perpendiculars must all pass through the centre of the eye, which he regards as the *centre of visible direction*. To me his arguments do not appear conclusive. Were this opinion true, the point M' of an arrow $M'N'$, figure 14, would be seen along the dotted line moP , appearing at a spot very remote from its real position. It seems more consistent with observation to take the centre of the crystalline lens, or rather of the collective humours of the eye regarded as one lens, as the centre of visible direction. Through that centre c , fig. 14, all the directions pass from each part of an image, and these cross each other: the lowest part of an image is the highest of the object, and the highest of the image the lowest of the object. It has been supposed that in infancy we actually see erect objects inverted, and only discover that they are not so by the habitual correction derived from experience; but this fallacy has been fully corrected by observation on persons born blind, who first obtained the power of vision when of an age to express what they saw.

The apparent size of objects depends on their distance from the eye. Let mc , nc , fig. 14, be rays from the extreme points of the

Fig. 14.



arrow MN , which cross within the eye at c : then the angle MCN is

termed the *visual angle*. Mere inspection of the figure shows that the larger that angle is, the greater will be the arc on the retina occupied by the image mn ; and also the greater that image, the greater will be the angle included by the lines of visible direction. The visual angle in fact varies exactly as the arc of the image; and as that angle may be found with sufficient accuracy by drawing lines from the eye to the extremities of an object, it affords a convenient expression for the length of the image: when the angles are small, the linear magnitudes of two objects are nearly in the same ratio as their visual angles. If a second arrow $m'n'$, twice as long as mn , be placed parallel to mn , and at double its distance from the eye, then, by the properties of similar triangles, their visual angles will be equal, and their apparent magnitudes identical. Conversely, if the two arrows be parallel, have the same visual angle or apparent magnitude, and one be twice as distant as the other, the more remote one must be twice as long as the other. The apparent magnitude of the *same* object at different distances may be inferred on the same principles. Thus if mn approach the eye, remaining upright all the time, the visual angle will enlarge, and at half the distance its length will appear double; or if mn recede from the eye, it will be seen under a smaller angle, and appear proportionally smaller, until at double the distance it will seem to be half of its original length. In fact, the apparent length of an object increases in the same ratio as its distance from the eye, or more strictly from the point c within the eye, decreases. A large object seems a mere speck at a great distance; and a minute object is invisible unless brought close to the eye. To bring an object near the eye is to magnify it. A tower which appears 100 feet high to a person 4 miles distant, will seem 200 feet at 2 miles, and 400 at 1 mile; and the type of a book which at 12 inches appears a line in length, will appear two lines at 6 inches. In these cases it is the *linear* magnitude which varies inversely as the distance: the superficial extent, or area, will vary inversely as the square of the distance.

The foregoing considerations account for many optical phenomena. Short-sighted persons see minute objects better than those who have a long sight, because, from the greater refractive power of their eyes (page 97), they can bring the object closer to the eye than those who are long-sighted, and therefore see it under a greater angle. But by aid of a convex lens a long-sighted person may attain the same end. Let him place the object in the focus of a con-

vex lens, and the eye at a distance behind convenient for receiving all the rays which pass through it: the diverging rays, rendered parallel by the lens, are readily formed by the eye into an image on the retina, and the object is seen under the same angle as though the eye had occupied the position of the lens. This arrangement is shown by figure 13, where MN is the object, AB the lens, and E the eye of the observer. If the focal distance of the lens be 1 inch, we gain the same advantage as though the eye itself were placed at one inch; and taking 6 inches as the shortest distance of distinct vision with the unaided eye, the apparent length of the arrow will be increased in the ratio of 1 to 6. With the lens of half an inch focus, the increase will be as $\frac{1}{2}$ to 6, or 1 to 12; and if the focus is $\frac{1}{10}$ th of an inch, the increase will be as $\frac{1}{10}$ to 6, or 1 to 60. Convex lenses are hence familiarly known by the name of *magnifying glasses*.

Convex lenses are similarly employed in the construction of compound microscopes and telescopes. In figure 13, let nm represent a small object formed by the lens ab into an enlarged image MN : that image may be viewed by the eye at the distance of 6 inches; but by interposing a second lens AB of 1 inch focal distance, the effect is the same as though the eye were at 1 inch, and thus the image is further increased in the ratio of 1 to 6. The lens AB is called the *eye-glass*, and ab the *object-glass*. Again, in a telescope, a large distant object is represented as a minute image, and so far its magnifying power depends on the eye being able to inspect a small image at 6 inches instead of the large object at a great distance. For instance, a tower 400 feet high, formed into an image 1 foot long, is thereby shortened 400 times; but as that image can be seen distinctly at the distance of $\frac{1}{2}$ a foot instead of the object at 400 feet, the elongation due to this cause alone is as 1 to 800. The apparent height of the tower is thus diminished 400 times by one cause, and increased 800 times by another; so that the compound effect is, that it is doubled. But by employing a second lens with a very short focus, the image may be still further magnified to a great extent.

Double Refraction.—If on a piece of paper with a black line on its surface we place a rhombohedron of Iceland-spar, and then look at the line through the crystal, it will be found that in a certain position the line appears single as when seen through water or glass; but in other positions of the crystal two lines are visible

parallel to each other, and separated by a distinct interval. The light in passing through the crystal is divided into two portions, one of which obeys the laws of refraction already explained (page 92); whereas the other portion proceeds in a wholly different direction, and hence gives the appearance of two objects instead of one. The former is termed the *ordinary*, the latter the *extraordinary* ray. This phenomenon is known by the name of *double refraction*, and has been witnessed in many crystallised substances, as in minerals and artificial salts.

Light transmitted through Iceland-spar or other doubly refracting substances, is found to have suffered a remarkable change. In this state it is distinguished from common light by the circumstance, that when it falls upon a plate of glass at an angle of $56^{\circ} 11'$, it is almost completely reflected in one position of the glass, and is hardly reflected at all in another: if reflected when the plane of reflection is vertical, no reflection ensues when the reflecting plane is horizontal, the incident angle being maintained at $56^{\circ} 11'$. This curious property, so different from common light, has been theoretically ascribed to a kind of *polarity* of such sort, that each side of a ray of light is thought to have a character different from the two adjacent sides at right angles to it; and hence the origin of the term *polarized light*, by which this property is distinguished. Light is polarized by reflection from many substances, such as glass, water, air, ebony, mother-of-pearl, and many crystallized substances, provided the light is incident at a certain angle peculiar to each surface, and which is called the *polarizing angle*. Thus, the polarizing angle for glass is $56^{\circ} 11'$, and for water $53^{\circ} 14'$; that is, common light reflected by glass and water at the angles stated will be polarized.

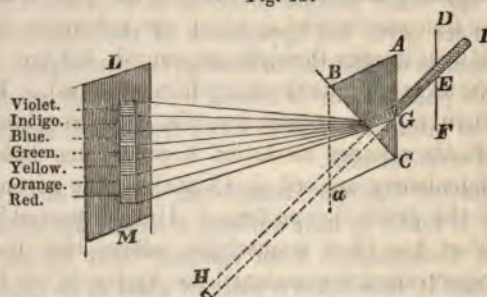
The phenomena of double refraction and polarized light constitute a department of optics of great and increasing interest; but it is too remote from the pursuits of a chemical student to be treated of at length in this work. Those interested in such studies will find an excellent guide in Brewster's Treatise on Optics in the Cabinet Cyclopædia.

DECOMPOSITION OF LIGHT.

The analysis of light may be effected either by refraction or absorption. Newton, who discovered the compound nature of solar light, effected its decomposition by refraction, employing a solid

piece of glass bounded by three plane surfaces, well known under the name of the *prism*. His mode of operating consisted in admitting a ray of light IC , fig. 15, into a dark chamber through

Fig. 15.



a window-shutter DEF , and interposing the prism ACB , so that the ray should pass obliquely through two surfaces, and be refracted by both. On receiving the refracted ray upon a piece of white paper LM , there appeared, instead of a spot of white light, an oblong coloured surface composed of seven different tints, called the *prismatic* or *solar spectrum*. On subjecting each of these colours to refraction no further separation was accomplished; but on causing the rays separated by one prism to pass through a second of the same power and in an inverted position cba , the seven colours disappeared, and a spot of white light appeared at H , in the very position which it would have occupied had both prisms been absent. From such and similar experiments Newton inferred that white light is a mixture of seven *colorific* rays, red, orange, yellow, green, blue, indigo, and violet; and that the separation of these primary or simple rays depended on an original difference of refrangibility, violet being the most refrangible and red the least so.

Though a prism is the most convenient instrument for decomposing light, the separation of the coloured rays is more or less effected by refracting media in general. Lenses, accordingly, disperse the colorific rays at the same time that they refract them; and this effect constitutes one of the greatest difficulties in the construction of telescopes, in so much as the separation or *dispersion*, as it is termed, of these rays diminishes the distinctness of the image. The combinations by which the defect is remedied are called *achromatic*.

Newton's analysis of light led him to explain the origin of the colours of natural objects. Of opaque bodies those are black which

absorb all the light that falls upon them, and those white which reflect it unchanged: the various combinations of tints are the consequence of certain rays being absorbed, while those alone whose intermixture produces the observed colour are reflected. The same applies to transparent media, which are colourless like pure water when the light passes through unchanged, but are coloured when some rays are transmitted and others absorbed. This absorption of certain rays by coloured media, such as glass of different tints, affords another mode of decomposing light; and Brewster has ingeniously applied it to analyse the seven colours which compose the prismatic spectrum. He has proved by such experiments, what has been maintained before, that the seven colours of the spectrum are occasioned not by seven, but by three simple or primary rays; namely, the red, yellow, and blue. These rays are concentrated in those parts of the spectrum where each primary colour respectively appears; but each spreads more or less over the whole spectrum, the mixture of red and yellow giving orange, of yellow and blue green, and red with blue and a little yellow causing the violet.

The prismatic colours, according to the experiments of Sir W. Herschel, differ in their illuminating power: the orange illuminates in a higher degree than the red, the yellow than the orange. The maximum of illumination lies in the brightest yellow or palest green. The green itself is almost equally bright with the yellow; but beyond the full deep green the illuminating power sensibly decreases. The blue is nearly equal to the red, the indigo is inferior to the blue, and the violet is the lowest on the scale. (Phil. Trans. 1800.)

Calorific rays in Light.—The solar rays, both direct and diffused, are capable of exciting heat. When reflected or transmitted, no such effect results: the concave reflector and burning-glass remain cool, though intense heat is developed at their foci; and the atmosphere is not heated by the solar rays to which it gives a passage. But opaque bodies which absorb light are invariably heated by it, and the temperature is proportional to the absorbent power. Hence, dark-coloured substances, which are more absorbent than light ones, become hotter when exposed to sunshine. This is attested by the general preference given to light-coloured clothing during summer. Hooke, and subsequently Franklin, proved the fact by exposing pieces of cloth of the same texture and

size, but different colours, upon snow to sunshine; when the snow under the dark specimens was found to melt more freely than under the light ones, the effect being nearly proportional to the depth of shade. Davy arrived at similar results. The coloured rays of the spectrum differ in heating power. This is shown generally by looking at the sun through glass of different colours, when it will be found that red and yellow glasses heat and oppress the eye much more than blue or green ones; but the fact was first rigidly demonstrated by Sir W. Herschel, by placing the bulb of a delicate thermometer in the coloured spaces of the solar spectrum. He found that it stood highest in the red space, fell lower and lower when successively removed towards the violet, and was lowest in the violet space. (Phil. Trans. 1800.)

The foregoing facts are explicable on the suppositions either that light is convertible into heat by absorption, or that heat is merely associated with light, and is absorbed along with it. Herschel maintained the latter view, and founded it on his observation that, though the red space of the spectrum is hotter than the other coloured spaces, there is a spot a little beyond the red, where little or no light appears, where the thermometer is higher than in the red itself. He hence inferred that there exists in the solar beam a distinct kind of ray, which causes heat but not light; and that these rays, from being less refrangible than the luminous ones, deviate in a smaller degree from their original direction in passing through the prism.

All succeeding experimenters confirm the statement of Herschel, that the prismatic colours differ in heating power; but they do not agree as to the spot where the heat is greatest. Englefield, Davy, and others affirmed with Herschel that it is beyond the red ray; while others, and in particular Leslie, contended that it is in the red itself. The observations of Seebeck (Edin. Journ. of Science, i. 358) explained these contradictory statements, by showing that the point of greatest heat varies with the kind of prism which is employed for forming the spectrum. When he used a prism of fine flint-glass, the greatest heat was uniformly beyond the red; with a prism of crown-glass, the red itself was the hottest part; and with a prism externally of glass, but containing water within, the maximum heat was neither in the red itself, nor beyond it, but in the yellow. These experiments have been confirmed by Melloni, who has succeeded with a prism of

rock-salt in separating the spot of maximum heat from the coloured part of the spectrum by a much greater interval than had been done previously, and dissipating all remaining doubt as to the existence in solar light of calorific rays distinct from those rays which produce colour. As in simple radiant heat (page 19), there exist in solar light calorific rays of different characters, some being more, some less, refrangible. The former are proportionally less absorbed by feebly diathermanous media than the latter; whereas good diathermanous media absorb the less refrangible more freely than the more refrangible rays. For instance, the heat of the violet passes through water more readily than that of the yellow space, that of the yellow than the red; but in employing media always rising in transalency, as crown-glass, flint-glass, and rock-salt, the obstruction to the least refrangible calorific rays continually decreases. Hence, in successively taking prisms of rock-salt, flint-glass, crown-glass, and water, the spot of greatest heat will be found first far beyond the red, then nearer the red, then in the red itself, and lastly in the yellow space of the spectrum. On using a prism still less transalcent than water, the maximum heat would be found on the violet side of the yellow space. By causing light, terrestrial as well as solar, to pass first through water, and then through glass coloured green by oxide of copper, Melloni so effectually absorbed all the calorific rays, that the issuing light did not affect the most delicate thermoscope. It would hence follow, not merely that light is associated with calorific rays quite distinct from the luminous rays, but that the latter contributes nothing to the heat evolved during its absorption.

Chemical rays.—Solar light is capable of producing powerful chemical changes. One of the most striking instances of it is its power of darkening the white chloride of silver; an effect which takes place slowly in the diffused light of day, but in the course of two or three minutes by exposure to sunshine. This effect was once attributed to the influence of the luminous rays; but Ritter and Wollaston traced it to the presence of certain rays that excite neither heat nor light, and which, from their peculiar agency, are termed *chemical rays*. The greatest chemical action is exerted just beyond or at the verge of the violet part of the prismatic spectrum; the spot next in energy is the violet itself; and the property gradually diminishes in advancing to the green, beyond which it seems wholly wanting. It hence follows that the che-

mical rays are still more refrangible than the luminous, in consequence of which they are dispersed in part over the blue, indigo, and violet, but in the greatest quantity at the extreme border of the latter.

Magnetizing rays.—The more refrangible rays of light were once thought to possess the property of rendering steel and iron magnetic; but since the experiments of Riess and Moser, this notion has been abandoned. (Brewster's Journal, II. 225.)

TERRESTRIAL LIGHT.

Under this head is included all kinds of artificial light. The common method of obtaining such light is by the combustion of inflammable matter, which gives out so much heat that the burning substance is rendered luminous in the act of being burned. All bodies begin to emit light when heat is accumulated within them in great quantity; and the appearance of glowing or shining, which they then assume, is called *incandescence*. The temperature at which solids in general begin to shine in the dark is between 600° and 700° ; but they do not appear luminous in broad daylight till they are heated to about 1000° . The colour of incandescent bodies varies with the intensity of the heat. The first degree of luminousness is an obscure red. As the heat augments, the redness becomes more and more vivid, till at last it acquires a full red glow. If the temperature still increase, the character of the glow changes, and by degrees it becomes white, shining with increasing brilliancy as the heat augments. Liquids and gases likewise become incandescent when strongly heated; but a very high temperature is required to render a gas luminous, more than is sufficient for heating a solid body even to whiteness. The different kinds of flame, as of the fire, candles, and gas light, are instances of incandescent gaseous matter.

Artificial lights differ in colour, and accordingly exhibit different appearances when transmitted through a prism. The white light of incandescent charcoal, which is the principal source of the light from candles, oils, and the illuminating gases, contains the three primary calorific rays, the red, yellow, and blue. The dazzling light emitted by lime intensely heated, first proposed by Lieut. Drummond for the trigonometrical survey (Phil. Trans. 1830), and of late so successfully applied by Messrs. Cooper and Carey for their gas microscope, gives the prismatic colours almost as

bright as in the solar spectrum. The light emitted by iron feebly incandescent consists principally of the red rays, as does the red light obtained by means of strontia and lithia; that from ignited boracic acid is such a mixture of the blue and yellow rays as constitutes green; and incandescent soda emits a yellow light, almost wholly free from the rays which cause the red and blue colours.

Artificial light differs from solar light in containing heat in two states. It contains simple radiant heat like that radiated from a body not luminous, and which may be separated by transmission through a plate of moderately thick glass; but the light so purified still heats any body which absorbs it, possessing calorific rays associated with its luminous rays like those in solar light (page 103,) and like them susceptible of refraction by transparent media. Thus, Daniell found that the rays from incandescent lime were concentrated by convex lenses, and set fire to phosphorus placed in the focus (Phil. Mag. N. S. 11. 59). Agreeably to the researches of Melloni (page 20,) artificial light contains different modifications of radiant heat, which not only differ in refrangibility, but in transmissibility through diathermanous media.

The chemical agency of artificial light is analogous to that from the sun. In general the former is too feeble for producing any visible effect; but light of considerable intensity, such as that from ignited lime, darkens chloride of silver, and seems capable of exerting the same chemical agencies as solar light, though in a degree proportionate to its inferior brilliancy. (An. of Phil. xxvii. 451.)

Light emanates from some substances either at common temperatures or at a degree of heat disproportioned to the effect, giving rise to an appearance which is called *phosphorescence*. This is exemplified by a composition termed *Canton's phosphorus*, made by mixing three parts of calcined oyster-shells with one of the flowers of sulphur, and exposing the mixture for an hour to a strong heat in a covered crucible. The same property is possessed by chloride of calcium (Homberg's phosphorus), anhydrous nitrate of lime (Baldwin's phosphorus), some carbonates and sulphates of baryta, strontia, and lime, the diamond, some varieties of fluor-spar called *chlorophane*, apatite, boracic acid, borax, sulphate of potassa, sea-salt, and by many other substances. Scarcely any of these phosphori act unless they have been previously exposed to light, though they do not always shine with light of the same colour as that

which excites the phosphorescence : for some, diffused daylight or even lamp-light will suffice ; while others require the direct solar light, or the light of an electric discharge. Exposure for a few seconds to sunshine enables Canton's phosphorus to shine in a dark room for several hours afterwards. Warmth increases the intensity of light, or will renew it after it has ceased ;—but it diminishes the duration. When the phosphorescence has ceased it may be restored, and in general for any number of times, by renewed exposure to sunshine ; and the same effect may be produced by passing electric discharges through the phosphorus. Some phosphori, as apatite and chlorophane, do not shine until they are gently heated ; and yet if exposed to a red heat, they lose the property so entirely that exposure to solar light does not restore it. Pear-sall has remarked that in these minerals the phosphorescence, destroyed by heat, is restored by electric discharges ; that specimens of fluor-spar, not naturally phosphorescent, may be rendered so by electricity ; and that this agent exalts the energy of natural phosphori in a very remarkable degree. (R. Inst. Journal, N. S. i.) The theory of these phenomena is obscure. Chemical action is not the cause, for these phosphori shine *in vacuo* or in gases which do not act chemically on them, and some even under water. It may be presumed that light causes in them a certain vibratory state analogous to that, though in a far lower degree, which exists in incandescent matter.

Another kind of phosphorescence is observable in some bodies when strongly heated. A piece of lime, for example, heated to a degree which would only make other bodies red, emits a brilliant white light of such intensity that the eye cannot support its impression.

A third species of phosphorescence is observed in the bodies of some animals, either in the dead or living state. Some marine animals, and particularly fish, possess it in a remarkable degree. It may be witnessed in the body of the herring, which begins to phosphoresce a day or two after death, and before any visible sign of putrefaction has set in. Sea-water is capable of dissolving the luminous matter ; and it is probably from this cause that the waters of the ocean sometimes appear luminous at night when agitated. This appearance is also ascribed to the presence of certain animalcules, which, like the glow-worm of this country, or the fire-fly of the West Indies, are naturally phosphorescent.

Light sometimes appears during the process of crystallization. This is exemplified by a tepid solution of sulphate of potassa in the act of crystallizing; and it has been likewise witnessed under similar circumstances in a solution of fluoride of sodium and nitrate of strontia. Another instance of the kind is afforded by the sublimation of benzoic acid. Allied to this phenomenon is the phosphorescence which attends the sudden contraction of porous substances. Thus, on decomposing by heat the hydrates of zirconia, peroxide of iron, and green oxide of chromium, the dissipation of the water is followed by a sudden increase of density suited to the changed state of the oxide, and a vivid glow appears at the same instant. The essential conditions are, that a substance should be naturally denser after decomposition than it was previously, and that the transition from one mechanical state to the other should be abrupt.

Instruments designed for measuring intensities of light are termed *photometers*. That of Leslie is the only one used to estimate the strength of the sun's light. It consists of his differential thermometer, with one ball made of black glass. The clear ball transmits all the light that falls upon it, and therefore its temperature is not affected; it is all absorbed, on the contrary, by the black ball, and by heating and expanding the air within, causes the liquid to ascend in the opposite stem. The whole instrument is covered with a case of thin glass, the object of which is to prevent the balls from being affected by currents of cold air. The action of this photometer depends on the absorption of the heat by which light is accompanied.

Leslie recommended his photometer also for determining the relative intensities of artificial light, such as that of candles, oil, or gas. This application of it differs from the foregoing, because light from terrestrial sources contains calorific rays of different properties; some being largely absorbed by glass, and others freely transmissible. The former, being for the most part arrested by the outer glass-case, will not cause any great error; but the latter must give rise to serious fallacies whenever the calorific and luminous rays of the two lights are not in the same ratio. This is rarely, if ever, the case with lights which differ in colour. Thus, the light emitted by burning cinders or red-hot iron, even after passing through glass, contains a quantity of calorific rays, which is out of all proportion to the luminous ones; and, consequently, they may

and do produce a greater effect on the photometer than some lights whose illuminating powers are far stronger.

A photometer on a different principle has been described by Rumford in his *Essays*. It determines the relative strength of lights by a comparison of their shadows, and is susceptible of great accuracy when employed with the required care; but,* like the foregoing, its indications cannot be trusted when there is much difference in the colour of the lights. In this case, the best procedure is, to observe the distance from each light at which any given object, as a printed page, ceases to be distinctly visible. The illuminating power of the lights so compared is as the squares of their distances.

ON THE RELATIONS OF HEAT AND LIGHT.

Radiant heat and light have the most intimate resemblance. They are distributed, reflected, refracted, absorbed, transmitted, polarized, according to laws so exactly parallel, as to force on the mind the conviction that their causes are likewise similar. If light be due to ethereal vibrations, it is difficult not to assign a similar cause to radiant heat. The obstacle to adopting this view arises from the peculiar relations of heat to matter as connected with change of form, with specific heat, and with heat of temperature. The outline of such an undulatory theory might be thus stated:—Heat may be considered identical with the universal ether, so that the terms ether and matter of heat would apply to the same substance. Diffused within the pores of bodies this ether causes the condition of temperature, and in a state of more intimate union it determines their form. Conduction may be due to a peculiar vibration of ether, advancing slowly among the molecules of matter, and modified by their presence,—a radiation from particle to particle. Common radiation of heat may be ascribed, not to the ether itself being ejected from a hot body; but to ethereal impulses originating in the same manner as those of light, but having waves of different grades both of length and intensity. It would not be prudent, however, at present to embody such a theory with the ordinary doctrines of heat, though as a scientific speculation it is a subject of great and increasing interest.

* See an Essay on the Construction of Coal Gas Burners, &c. in the *Edinburgh Philosophical Journal* for 1825.

SECTION III.

ELECTRICITY.

Elementary Facts.—When certain substances, such as amber, glass, sealing-wax, sulphur, are rubbed with dry silk or cloth, they are found to have acquired a property, not observable in their ordinary state, of causing contiguous light bodies to move towards them; or if the substances so rubbed be light and freely suspended, they will move towards contiguous bodies. After a while this curious phenomenon ceases; but it may be renewed an indefinite number of times by friction. The principle thus called into action is known by the name of *electricity*, from the Greek word *ηλεκτρον*, amber, because the electric property was first noticed in it. The same term is applied to the science which treats of the phenomena of electricity.

When a substance by friction or any other means acquires the property just stated, it is said to be *electrified*, or to be *electrically excited*; and its motion towards other bodies, or of other bodies towards it, is ascribed to a force called *electric attraction*. But its influence, on examination, will be found to be not merely attractive; on the contrary, light substances, after touching the electrified body, will be disposed to *recede* from it just as actively as they approached it before contact. This is termed *electric repulsion*. By aid of the electrical machine, electric attraction and repulsion may be displayed by a great variety of amusing and instructive experiments, showing how readily an invisible power is called into operation, and how wonderfully inert matter is subject to its control. But the student may witness these effects quite satisfactorily by very simple apparatus. Let him suspend a thread of white sewing silk from the back of a chair so that one end may hang freely, taking the precaution to moisten that end slightly by holding it between the fingers, while the rest of the thread is carefully dried by the fire; and let him then place near the free end of a piece of sealing-wax previously rubbed on the sleeve his coat. The silk will move towards it; but after touching the excited wax two or three times, it will recede from it.

When an electrified body touches another which is not electri-

fied, the electric property is imparted by the former to the latter. Thus, on touching the free end of the suspended silk thread with the excited wax, the silk will itself be excited, as shown by its moving towards a book, a knife, or other unexcited object placed near it. But although electricity is always imparted by an excited to an unexcited body by contact, the latter does not always exhibit electric excitement. If, for example, the suspended silk be wetted along its whole length, it will be strongly attracted by the excited wax, but after contact it will not evince the least sign of being itself electrified. Nevertheless, electricity is communicated to the silk in both cases; only it is retained by silk when dry, and is lost as soon as received by wet silk. Such observations led to the discovery that electricity passes with great ease over the surface of some substances, and with difficulty over that of others, and hence to the division of bodies into *conductors* and *non-conductors* of electricity. If electricity be imparted to one end of a conductor, such as a copper wire, the other extremity of which touches the ground, or is held by a person standing on the ground, the electricity will pass along its whole length and escape in an instant, though the wire were several miles long; whereas excited glass and resin, which are non-conductors, may be freely handled without losing any electricity except at the parts actually touched. To the class of conductors belong the metals, charcoal, plumbago, water, and aqueous solutions, and substances generally which are moist or contain water in its liquid state, such as animals and plants, and the surface of the earth. These, however, differ in their conducting power: of the metals, Harris found silver and copper to be the best conductors; and after these follow gold, zinc, platinum, iron, tin, lead, antimony, and bismuth (Phil. Trans. 1827). This order, as Forbes has remarked, is nearly that of their conducting powers for heat. Aqueous solutions of acids and salts conduct much better than pure water. To the list of non-conductors belong glass, resins, sulphur, diamond, dried wood, precious stones, earth and most rocks when quite dry, silk, hair, and wool. Air and gases in general are non-conductors if dry, but act as conductors when saturated with moisture.

This knowledge is of continual application in electrical experiments. When it is wished to collect electricity on a metallic surface, the metal must be *insulated*, that is, cut off from contact with the earth, and with conductors touching the ground, by means

of some non-conductor; an object commonly effected either by supporting it on a handle of glass, or by placing it on a stool made with glass feet. Another mode of insulating is to suspend a substance by silk threads. But such insulators must be dry; since they begin to conduct as soon as they grow damp, and conduct well, as in the experiment above described, when wet. Again, electrical experiments are very apt to fail in damp weather, because the moisture both carries off electricity directly, and by being deposited on the glass supports destroys the insulation.

To diminish this inconvenience it is usual to keep the insulators warm, and to coat them with a varnish made by dissolving the resin called shell-lac in alcohol, this resinous matter being much less prone to attract moisture from the air than glass. The same principles account for an error once prevalent that a metal cannot be excited by friction: if held in the hand, indeed, it exhibits no sign of excitement when rubbed, because the electricity is carried off as soon as excited; but if, while carefully insulated, it is rubbed with a dry cat's fur, excitement readily ensues.

On comparing the electric properties manifested by glass and sealing-wax when both are rubbed by a woollen or silk cloth, they will be found essentially different; hence it is inferred that there are two kinds or states of electricity, one termed *vitreous*, because developed on glass, and the other *resinous* electricity, from being first noticed on resinous substances. These two kinds of electricity, one or other of which is possessed by every electrified substance, are also termed *positive* and *negative*, the terms *vitreous* and *positive* being used synonymously, as are *resinous* and *negative*: they are also denoted by the signs + and -. If two electrified substances are both positive or +, or both negative or -, they are invariably disposed to recede from each other, that is, to exhibit electric repulsion; but if one be +, and the other -, their mutual action is as constantly attractive. The end of a silk thread, after contact with an electrified stick of sealing-wax, is repelled by the wax, because both are -; but a dry warm wine-glass, if rubbed with cloth or silk, will be +, and if then presented to the thread, attraction will ensue. A silk thread, in a *known* electric state, thus indicates the kind of electricity possessed by other substances: a convenient mode of doing this, is to draw a thread of white silk rapidly through a fold of coarse brown paper previously warmed, by which means its whole length will be rendered +.

When two substances are rubbed together so as to electrify one of them, the other, if in a state to retain electricity, will be excited also, one being always —, and the other +. It is easy to be satisfied of this by very simple experiments. Rub a stick of sealing-wax on warm coarse brown paper, and the paper will be found to repel a positively excited thread of silk, while the wax will attract it; if a warm wine-glass be rubbed on the brown paper, the glass will be +, as shown by its repelling the + thread, while the same thread will be attracted by the — paper; friction of sealing-wax on a silk riband renders the wax — and the riband +, but with glass the riband is —. If two silk ribands, one white and the other black, be made quite warm, placed in contact, and then drawn quickly through the closed fingers, they will be found on separation to be highly attractive to each other, the white being +, and the black —. The back of a cat is + to all substances with which it has been tried, and smooth glass is + to all except the back of a cat. Sealing-wax is — to all the substances just enumerated, but becomes + by friction with most of the metals. The reader will perceive from these facts that the same substance may acquire both kinds of electricity, becoming + by friction with one body, and — with another.

THEORIES OF ELECTRICITY.

The nature of electricity, like that of heat, is at present involved in obscurity. Both these principles, if really material, are so light, subtile, and diffusive, that it has hitherto been found impossible to recognise in them the ordinary characteristics of matter; and therefore electric phenomena may be referred, not to the agency of a specific substance, but to some property or state of common matter, just as sound and light are produced by a vibrating medium. But the effects of electricity are so similar to those of a mechanical agent—it appears so distinctly to emanate from substances which contain it in excess, and rends asunder all obstacles in its course so exactly like a body in rapid motion, that the impression of its existence as a distinct material substance *sui generis* forces itself irresistibly on the mind. All nations, accordingly, have spontaneously concurred in regarding electricity as a material principle; and scientific men give a preference to the same view, because it offers an easy explanation of phenomena, and suggests a natural language easily intelligible to all.

Theory of two Electric Fluids.—This theory, the fundamental facts of which were supplied partly by Dufay, and partly by Symmer, is founded on the assumed existence of two electric fluids, which Dufay distinguished by the terms *vitreous* and *resinous* electricity. In order to account for electric phenomena by this supposition, the two fluids are assumed to possess the following properties:—They are both equally subtle and elastic, universally diffused and therefore present in all bodies, possessed of the most perfect fluidity, each highly repulsive to its own particles, and as highly attractive to those of the opposite kind, these attractive and repulsive forces being exactly equal at the same distance, and both varying inversely as the square of the distance varies. Electric quiescence is ascribed to these fluids being combined and neutralized with each other; and electric excitation is the consequence of either fluid being in excess. Their combination is destroyed by several causes, of which friction is one. The application of these principles is as follows. Two unexcited contiguous bodies, A and B, are electrically indifferent to each other; for, though each electricity in A repels the electricity of the same name in B, attraction to precisely the same extent is exerted between the opposite electricities, and no change results. If A and B are rubbed together, a portion of the combined electricities in both is decomposed, and the separated resinous fluid is transferred to one of them, suppose to A, and the vitreous to B, each being electrified to the same degree, though oppositely. The free particles of resinous electricity in A tend by their repulsion to recede from each other, and would quit A altogether, unless their passage were impeded by a non-conductor: the atmosphere, if dry, cuts off the retreat, and by its pressure confines the resinous fluid to the surface of A. The same happens to the vitreous fluid on the surface of B. But the opposite electricities fixed on A and B exert a strong mutual attraction, and may succeed either in forcing their way across the intervening stratum of air, or of actually drawing A and B into contact. In either case the free electricities reunite, and the electric equilibrium is restored. On the contrary, if A and B are similarly electrified, that is, possess the same kind of free electricity, the effort of the electric fluid to escape in opposite directions causes the substances themselves to fly asunder, if the repulsive force exceed their weight, and thus produces electric repulsion.

This theory, as commonly stated, takes little or no cognizance of

any attraction between the electric fluids and other material substances. But it would be against all analogy to suppose no such influence to exist; and indeed the supposition of an attractive force acting at insensible distances seems necessary to account for the impediment caused by non-conductors to the free movement of the electric fluids.

Theory of a single Fluid.—The celebrated American philosopher, Franklin, proposed a different theory, founded on the supposition of a single electric fluid, the particles of which are conceived to repel each other with a force diminishing as the squares of the distance, and to be attracted by matter in general according to the same law. Material substance in its unelectric state is regarded as a compound of electricity and matter, saturated and neutralized with each other. It is also an assumption, shown to be necessary by *Æpinus* and *Cavendish*, that ponderable bodies repel each other with the same force and according to the same law as the particles of electricity. From the nature of these postulates it will be easy to anticipate their application. Unelectric bodies are such as have their natural quantity of electricity, which precisely suffices to saturate and neutralize the matter of which they consist. They are then electrically indifferent; because the repulsion exerted between the electricity and matter of contiguous bodies is exactly counteracted by the attraction of the electric fluid in each for the matter of the other. Electrical excitement is occasioned either by increase or diminution of the natural quantity of electricity. On rubbing a tube of glass with a woollen cloth, the electric condition of both is disturbed: the glass acquires more electricity than it naturally possesses, or is overcharged with electric fluid; and the cloth, losing what the glass gained, contains less than its natural supply, or is under-charged. These opposite states are denoted by the algebraic terms *positive* and *negative*; the former corresponding to the vitreous, the latter to the resinous electricity of *Dufay*. Bodies positively excited, repel each other by reason of the repulsion among the particles of the electricity with which they are surcharged; and the equal tendency of negatively excited bodies to separate is ascribed to the mutual repulsion among the particles of matter. The electric equilibrium in excited substances is restored by the electricity escaping from those where it is in excess, and passing to those which are under-charged.

To the theory of Franklin it is usually objected that it involves

an assumption at variance with the laws of gravitation, namely, that of matter being repulsive to itself; but this objection is unfounded, as the laws of gravitation have been investigated for matter only when in its ordinary state, and probably do not apply in cases of electric excitement. The researches of Mossotti on the forces which regulate the internal constitution of bodies amply justify this conclusion. Adopting with Franklin a single electric fluid, he has shown that gravitation is perfectly consistent with the supposition that the molecules of matter are repulsive to each other: for were the repulsive force exerted between molecules of matter but slightly less powerful than the attraction of electricity for matter, or than the mutual repulsion of the atoms of the electric fluid, gravitation would be an immediate consequence of electric equilibrium. He has supported this opinion by a mathematical investigation of the conditions of equilibrium both for the molecules of matter and for the electric fluid. The results at which he arrived show that two molecules of matter surrounded by their electric atmospheres, are mutually attractive when separated by a sensible distance;—that the attraction increases on the approach of the atoms up to a certain point, where the attractive force attains its maximum, and beyond which the molecules are mutually repulsive. In this manner, gravitation, cohesion, and the resistance of matter to compression, are attributed to the same forces. These views certainly afford a happy explanation of the molecular mechanism; but as they have not yet been sufficiently tested, I shall retain the theory of the two electricities, which was adopted in former editions, substituting however, agreeably to present usage, the terms positive and negative, for vitreous and resinous electricity.

CAUSES OF ELECTRIC EXCITEMENT.

Friction.—This cause of electric excitement having been already mentioned, it here only remains to state the usual modes of developing electricity by friction. A supply of negative electricity is easily obtained by rubbing a stick of sealing-wax, or a glass tube covered with sealing-wax, with silk or woollen cloth; and positive electricity is freely developed when a dry glass tube is rubbed with silk, brown paper, or flannel, the surface of which is covered with a little amalgam. But for obtaining an abundant supply of electricity it is necessary to employ an electrical machine, which is a mechanical contrivance for exposing a large

surface of glass to continuous friction. As now constructed, it is formed either with a cylinder or plate of glass which is made to revolve upon an axis, and pressed during rotation by cushions or rubbers made of leather stuffed with flannel, and covered usually with silk. On the rubber is spread an amalgam of tin and zinc, rendered adhesive by admixture with a small quantity of lard or tallow. To prepare the amalgam, melt in a Hessian crucible one ounce of tin and three of zinc, then add two ounces of mercury heated to near its boiling point, stir briskly with a stick for a few minutes, and pour the mixture on a clean dry stone: when cold, pulverize and sift, and preserve the fine powder in a well-corked dry phial. Another essential part of the machine is the *prime conductor*, which is an insulated conductor, commonly made of brass, placed in such immediate proximity to the revolving glass, that the electric state of the one is instantly imparted to the other.

The electricity developed by the electrical machine is due partly to friction, which disunites the combined electric fluids of the glass and rubber, but principally to the oxidation of the amalgam. The positive fluid is transferred to the glass, from it to the contiguous prime conductor, and thence to any system of conductors connected with the prime conductor; and similarly the negative fluid collects upon the rubber, whence it is distributed to one or more conductors with which the rubber may be in connexion. Thus all insulated conductors in contact with the prime conductor are +, and those attached to the rubber are —. When once the glass and rubber are excited, it is necessary that the electric equilibrium of both should be restored before a second development can occur; and accordingly it is found that very little electricity is obtained when the prime conductor and rubber's conductor are both insulated. On taking + electricity from the prime conductor, the rubber should communicate with the ground, that its — electricity may escape; and when — electricity is taken from the rubber's conductor, the prime conductor is connected with the ground. The same object may be accomplished by connecting the prime conductor with the rubber's conductor, though in experiments it is commonly inconvenient to employ this arrangement.

Change of temperature.—The operation of this cause of electric excitement was first noticed in certain minerals, such as tour-

malin and boracite, not possessed of that symmetric arrangement of parts commonly observed in crystals, and which are electrified by the application of heat. But a far more general principle was detected by Seebeck, who found that the electric equilibrium is disturbed in certain metallic rods or wires when one extremity has a different temperature from that of the other, whether the difference be effected by the application of heat or cold. This observation has been since shown by Cumming to be true of all metals (*An. of Phil. N. S.* v. 427); and the same subject has been examined by Prideaux (*Phil. Mag. and An.* iii.). The experiment is usually made by heating or cooling the point of junction of two metallic wires, which are soldered together; but Becquerel has proved that the contact of different metals is not essential. (*An. de Ch. et Ph.* xli. 353.)

Chemical action.—Another, and perhaps by far the most fertile, source of electricity is chemical action. This was strongly denied by Davy in his Bakerian lecture for 1826; but the experiments of Becquerel, De la Rive, and Pouillet, afford decisive proof that chemical union and decomposition are both attended with electrical excitement (*An. de Ch. et Ph.* vol. 35, 36, 37, 38, and 39). Pouillet, in particular, has demonstrated that the gas arising from the surface of burning charcoal is +, while the charcoal itself is —; and he has proved that similar phenomena are produced by the combustion of hydrogen, alcohol, oil, and other inflammables of the same kind. In all these instances the combustible, in the act of burning, renders contiguous particles —; while the oxygen imparts + electricity to the products of combustion. The fact, with respect to charcoal, was originally noticed by Volta, La Place, and Lavoisier, but was subsequently denied by Saussure and Davy. Pouillet has reconciled these conflicting statements by showing that the result depends on the mode in which the experiment is conducted. For if the carbonic acid be completely removed from the burning mass at the instant of its formation, both are found to be electrical; but if the carbonic acid subsequently flow over the surface of the charcoal, the equilibrium will instantly be restored, and no sign whatever of excitement be perceptible. Decisive evidence of the same kind is supplied by the amalgam of the electrical machine, the influence of which is proportional to the degree of chemical action, and which ceases to be useful as soon as the metals are oxidized.

Thus, Wollaston found that amalgams of silver and platinum, which are indisposed to oxidize, are of no use when applied to the rubber; and that an amalgam of zinc and tin, which is the most oxidable, is also the best amalgam for exciting the machine. He observed that a machine in good action ceased to act when surrounded with carbonic acid, but instantly recovered its action on readmitting the air (Phil. Trans. 1801). On such facts is founded the foregoing statement, that the energy of the electrical machine is much more owing to chemical action than to friction.

Contact.—Another reputed source of electricity is contact of different substances, especially of metals; a source originally suggested by Volta, who founded on it a theory of galvanism. The facts on which Volta rested his opinion were of this nature. Well-cleaned plates of zinc and copper were furnished with glass handles, by which they could be both supported and insulated: the zinc plate, held by its glass handle, was laid repeatedly on the copper, which at the time need not be insulated, and after each contact the zinc was made to touch the instrument, shortly to be described, called the *condenser*. A + charge was gradually accumulated; and on operating in the same manner with an insulated plate of copper, it was found to communicate a - charge. He also stated that if one end of a zinc plate communicate with the condenser, while the zinc at its other end is in contact with a plate of copper, a + charge is communicated; and that - electricity is indicated when a copper plate, in contact with zinc at one end, rests at its other upon the condenser. From such experiments it was inferred, that the contact of zinc and copper disturbs the electric equilibrium in both metals, the latter acquiring an excess of - and the former of + electricity.

The quantity of electricity developed by contact is confessedly so small, that it requires for its detection the aid of very delicate instruments and of very careful manipulation; and the opinion is daily gaining ground that mere contact is incapable of causing electric excitation. The phenomena referred by Volta to contact, are ascribed by others to chemical action and to friction. De la Rive contends (An. de Ch. et Ph. xxxix. 297; lxii. 147), that the feeble charge commonly observed from the contact of zinc and copper, is due to slight oxidation caused by moisture and oxygen of the air acting on the plate of zinc. When he prevented such oxidation by operating in an atmosphere of

hydrogen or nitrogen, no electric excitement followed; and when he purposely increased chemical action, as by exposing the zinc to acid fumes, or by substituting for zinc a more oxidable metal, such as potassium, the electrical effects observable on contact with copper were greatly augmented. Electric excitation and chemical action were observed to be strictly proportional to each other. Again, Parrot of St. Petersburg (*An. de Ch. et Ph.* xlv. 361) not only confirms the statements of De la Rive, but shows that in those instances where electric excitement has been witnessed under circumstances which appear to exclude chemical action, the phenomenon may be ascribed to friction of the metals. He gives as the result of numerous experiments made with strict care, that the contact of zinc and copper, if unattended by friction or chemical action, causes not the least developement of electricity. The opposite evidence adduced by Volta and others must therefore, I apprehend, be rejected; and the only remaining facts in favour of Volta's opinion are derived from certain chemical agencies evinced by metals during contact, a subject which will be discussed in the section on galvanism.

Changes of form.—The changes of form caused in a substance by variations of temperature, such as liquefaction and solidification, the formation and condensation of vapour, constitute another reputed source of electricity. On liquefying sulphur in a glass vessel, and removing the cake after cooling, the sulphur is found to be — and the glass +; and on pouring water into a hot iron vessel or on a hot coal communicating with a delicate electrometer, the rapid evaporation of the water is attended with decisive indications of electrical excitement. To processes of this nature, continually taking place in the atmosphere, the electricity of the clouds is generally ascribed. But the opinion is questioned by Pouillet, who has shown that in most of the experiments adduced in its favour, chemical actions ensue at the same time, and that the greatest part of the effect is due to such changes. If, for example, evaporation be accompanied by chemical decomposition, as when saline solutions are evaporated, the water being separated from the salt with which it was previously united, or if the vessel consist of iron or other easily oxidable material, which is more or less chemically attacked by the evaporating water, then the developement of electricity is very decisive; but he contends that pure water evaporated in a clean platinum vessel gives rise to no

electrical excitement whatever. From such experiments Pouillet concludes that the electricity, hitherto referred to changes of form, is entirely owing to the chemical action by which they are generally attended; and these phenomena, of which evaporation from the ocean, rivers, and the surface of the earth, affords an instance, pure water being thereby separated from its saline impregnation, as also the chemical changes attendant on the growth and nutrition of plants, he regards as a fertile source of atmospheric electricity (*An. de Ch. et Ph.* xxxv. 401, and xxxvi. 5). In these views there is much truth. I have repeatedly noticed free electric excitement on pouring a solution of chloride of sodium or sulphate of soda into a heated platinum crucible, and also when pure water was dropped on red-hot iron or a glowing cinder; but I have as constantly failed of procuring any indication when pure water was evaporating on platinum. Harris, however, with an apparatus of unusual delicacy, finds evaporation of pure water from platinum to be attended with distinct development of electricity.

Proximity to an electrified body.—It is a direct consequence of the attractive and repulsive powers ascribed to the electric fluids, that an unelectrified conductor must be excited by the vicinity of an electrified body. Let *AB*, fig. 1, be an unexcited conductor, supported on an insulating glass rod *bc*; and let *c*, containing free + electricity, and similarly insulated, be placed near it on the side *A*.

Fig. 1.



The free + electricity on *c* will both repel the + fluid of *AB*, and attract its - fluid, and the result of these concurring forces is instantly to decompose a portion of the combined electricities of *AB*, the free - fluid approaching as close as possible to *c*, and the + fluid receding from it. The opposite ends of the conductor *AB* are thus oppositely electrified, and in an equal degree: the excitement is found, as would be anticipated, to be greatest at the extremities, and to diminish gradually towards the middle line *ab*, which is neutral. The quantity of electricity thus set free depends on the extent to which *c* is excited, and on its distance from *AB*. If now *c* be suddenly withdrawn, the opposite fluids at *A* and *B* coalesce, and the equilibrium of *AB* is restored. But so long as *c* retains its position, *A* will be -, even were it uninsulated. The only effect of communication with the ground is to neutralize the + fluid at *B* by supplying to it - electricity from the earth: if after

having effected this by touching the cylinder for an instant with the finger, *c* be withdrawn, *AB* is left with an excess of the — fluid.—The electricity thus developed by the contiguity of an electrified body is said to be *induced*, or to be excited by *induction*.

The student should reflect carefully on these inferences from the theory of electricity, since the applications of such knowledge are numerous. A few of these may now be enumerated :—

1. An electrified body attracts light objects near it, because it induces in them a state opposite to itself. The attraction is most lively when the light object is a conductor, and in contact with the ground, since it then more completely assumes an electric state opposed to that of the inducing body. A non-conductor is very imperfectly electrified by induction, because the electric fluids cannot quit each other from inability to move through the non-conductor.

2. If a stick of sealing-wax, strongly — be presented to a thread or pith ball which is also negatively, but feebly, excited, repulsion will ensue at a considerable distance, followed by attraction when the distance is small. This attraction is due to the strongly excited wax acting by induction on the feebly — thread, thereby causing it to have an excess of + electricity.

3. The + electricity collected on the prime conductor of an electrical machine is by some ascribed, not to a transfer of that fluid from the glass to the prime conductor, but to a part of the combined electricities of the prime conductor being separated by induction, and the — fluid being imparted to the + glass. The same view is applicable to any system of conductors in contact with the prime conductor, as also to conductors connected with the rubber. It is difficult to say which explanation is the more correct, or whether both may not be true.

4. On moving the hand towards the prime conductor of an excited electrical machine, the hand becomes — by induction, and the spark ultimately obtained restores the equilibrium. In like manner a negatively electrified cloud renders + a contiguous tree or tower, and then a stroke of lightning follows as a consequence of attraction between the two accumulated fluids.

5. The action of the *Leyden jar* depends on the principle of induced electricity. A glass jar or bottle with a wide mouth is coated externally and internally with tinfoil, except to within three or four inches of its summit; and its aperture is closed by dry wood or some imperfect conductor, through the centre of which

passes a metallic rod communicating with the tinfoil on the inside of the jar. On placing the metallic rod in contact with the prime conductor of an excited electrical machine, while the outer coating communicates with the ground, the interior of the jar acquires a charge of + electricity, and the exterior becomes as strongly —. If, the jar being insulated, the metallic rod be placed close to the prime conductor, avoiding actual contact, while an uninsulated conductor be held at an equal distance from the outer coating, electric sparks in equal number and of equal size will pass between both intervals, and both sides of the jar are found to be in the same condition as before; but no charge will be received when the inner coating communicates with the prime conductor, and the outer coating is strictly insulated. From these facts it is inferred that the interior of the jar becomes +, either by receiving + electricity directly from the prime conductor, or, as is more probable, by communicating to it — electricity; and that the exterior then becomes — by the loss of a quantity of + electricity, equal to that on the interior. Unless means be afforded for the escape of the + electricity from the exterior, no charge ought to be received; and this conclusion is quite conformable to the fact above stated.

The opposite electric fluids accumulated on the opposite sides of a charged Leyden jar exert a strong mutual attraction through the substance of the glass, and the presence of either secures the continuance of the other. The exterior of the jar may be freely handled, and its coating removed, without destroying the charge, provided no communication be made at the same time with the interior; and if the exterior be insulated, the charge will be preserved, though the tinfoil of the interior be removed. But when a conductor communicates with both surfaces at the same instant, the two fluids rush together with violence, and the equilibrium is restored. Whether in this and similar cases the two fluids coalesce entirely on the intermediate conductor, or whether each from its velocity may not in part pass the other, and be projected to the opposite surface, is a question on which electricians are not agreed.

The Leyden jar affords the means of passing through bodies a large quantity of electricity. For not only may jars of any required size be employed, but it is easy so to arrange any number of such jars, that they shall all be charged and discharged at the

same time, constituting what is termed an *electrical battery*. The arrangement is made by placing a number of Leyden jars in a box lined with tinfoil, by which means their outer surfaces have free metallic communication with each other, and connecting their inner surfaces by wires.

The explanation above given of the action of a Leyden jar suggests a curious point of theory. A jar after it has been discharged contains a smaller quantity of the combined fluids than before it was charged, since the act of charging is ascribed to loss of $-$ electricity by the inner and of $+$ electricity by the outer surface of the jar, which loss is not restored at the moment of the discharge. Hence, if the same jar were charged and discharged many times in succession, the total quantity of electricity remaining in the jar ought to be diminished: and yet a Leyden jar does not seem to be impaired by use, but is equally effective at last as at first. Several kinds of assumption may be made to explain this.

1. The quantity of electricity present in bodies may be so enormous, that any loss obtained in our experiments is inappreciable.
2. There may be some unknown mode by which electricity abstracted from a substance is restored to it.
3. It may be that when the total quantity of electricity in a jar is diminished to a certain extent, the excited prime conductor no longer charges the interior by decomposing its combined fluids, but by imparting to it $+$ electricity; and that the outer surface of the jar is then supplied with a corresponding quantity of $-$ electricity directly from the earth.

6. The principle of induced electricity was ingeniously applied by Volta in the construction of the *Condenser*. This apparatus, fig. 2, consists of two brass plates, A and B, supported on a common stand D. One of the plates B is attached to the stand by means of a hinge C, so that, though represented upright, it may be placed horizontally, and be thus withdrawn from the vicinity of the plate A, the support of which is made of glass. On electrifying the insulated plate positively, the plate B, expressly placed close to A, is rendered $-$ by induction; and, as happens in the Leyden jar, the excitement of B will be proportional to that of A. The $-$ charge of B tends to preserve the $+$ charge of A, which may consequently receive still more electricity by contact

Fig. 2.



with any + surface, without losing what it had previously acquired. Thus is electricity accumulated or *condensed* on A; so that a substance too feebly excited to produce any appreciable effects of itself, may by repeated contact with the insulated plate of a condenser communicate a charge of considerable intensity. The effect of the accumulation is made apparent by withdrawing B, and bringing A in contact with a delicate electrometer. The condenser is much employed in experiments of delicacy, and the plate A is often permanently fixed on the gold leaf electrometer.

7. The *Electrophorus* is another contrivance of Volta's, which acts by induced electricity. It consists essentially of two parts; one being a flat cake of resin, made by pouring melted resin into a shallow plate or circular dish of tinned iron, and the other a disk of brass, of rather smaller diameter than the resin, supplied with a glass handle. The surface of the resin is negatively excited by friction or flapping with silk or flannel, and the brass disk is laid upon it. The resin being a non-conductor retains its own electricity in spite of the super-imposed brass, and decomposes the combined electricities of the latter, causing its under surface to be +, and its upper —. On touching the brass with the finger, its upper surface is neutralized; and on then withdrawing the brass plate, it is found to have an excess of + electricity. On replacing the brass as before, the resin, having lost none of its electricity in the process, acts again upon the metallic disk as on the first occasion, and will continue so to act for an indefinite number of times. Kept in a dry place, the electrophorus will keep in action for months.

ELECTROSCOPES AND ELECTROMETERS.

It is very important, in experiments on electricity, to possess easy methods of discovering when a substance is electrified, of ascertaining its *intensity* or the degree to which it is excited, and distinguishing the kind of excitement. The means for effecting these objects are founded on electrical attraction and repulsion, and the instruments employed for the purpose are called *Electroscopes* and *Electrometers*; the latter denoting the intensity of electricity,—the former merely indicating excitement, and the electrical state by which it is produced. The term electrometer, however, is often indiscriminately applied to all such instruments, since the methods of ascertaining the kind of excitement give at the same time some idea of its intensity.

Gold Leaf Electrometer.—Several simple electroscopic methods have already been indicated (page 114). Small balls made of the pith of elder are used for the same purpose. A single pith ball, suspended by a cotton thread, is attracted by a feebly electrified substance. Also, when two pith balls are suspended from the same point by cotton threads of equal length, and an electrified body is placed near them, the two balls are thrown by induction into the same electric state, and diverge. The gold leaf Fig. 3. electrometer, figure 3, invented by Bennett, acts upon the same principle, but is far more delicate. It consists of a glass cylinder cemented below upon a brass plate *cd*, and covered above by a brass plate *ab*, pierced in its centre for the insertion of a glass tube *bc*, the top of which is closed by a brass plate *a*: into this plate is screwed a thick brass wire, which passes through the glass tube, and from the lower end *d* of which two slips of gold leaf are suspended. These different parts are put together while quite dry, all the joinings are secured by wax cement, and the glass is covered by lac varnish. The effect of these arrangements is to insulate the plate *a* with its wire and gold leaves, while the latter are secure against being moved by currents of air. The approach of any electrified body, even though feebly excited, to the plate *a*, is immediately detected by the divergence of the leaves, as shown in the figure. The instrument is equally useful in indicating the kind of excitement, provided the plate and leaves be permanently electrified, which may easily be done on the same principle as in charging the metallic disk of an electrophorus. Thus, on placing a negatively excited body, as a stick of sealing-wax after friction on woollen cloth, near the brass plate of the electrometer, the electric equilibrium of its whole metallic surface is disturbed: the brass plate becomes +, and the slips of gold leaf diverge from being —. If the plate be then touched with the finger, the equilibrium of the gold leaves is restored, and their divergence ceases, while an excess of + electricity is preserved on the plate by the vicinity of the — sealing-wax. On removing *first* the finger, and *then* the sealing-wax, the brass is left with an excess of + electricity, which extends over the whole metallic surface of the electrometer, and thus produces a divergence which continues for a considerable time if the glass be dry, and the atmosphere moderately free from moisture. The approach to the brass plate of a positively excited body increases the divergence



of the gold leaves; because the plate becomes — by induction, and the + fluid retiring to the extremities of the leaves, renders them still more +. A negatively excited body has an exactly opposite effect, by attracting the + fluid towards the plate and from the leaves, and diminishing divergence.

Quadrant Electrometer.—An instrument much used for estimating the degree or intensity of electricity is the *quadrant electrometer*, figure 4, invented by Henley. It consists

of a smooth round stem of wood *ab*, about seven inches long, to the upper part of which, and projecting from its side, is attached a semicircular piece of ivory. In the centre *c* of the semicircle is fixed a pin, from which is suspended, to serve as an index, a slender piece of wood or cane *de*, four inches in length, and terminated by a small ball. When the apparatus is screwed on the prime conductor of the electrical machine, or placed on any electrified body, it indicates differences of electric intensity by the extent to which the index recedes from the stem; and in order to express the divergence in numbers, the lower half of the semicircle, which is traversed by the index, is divided into 90 equal parts called *degrees*. This instrument, though convenient for experiments of illustration, is not suited to those of research, wherein the object is to examine the effects of substances feebly electrified, and ascertain their relative forces with accuracy.



Fig. 4.

Torsion Electrometer.—This instrument, invented by Coulomb, is peculiarly fitted for scientific investigation. It consists of a small needle of gum-lac *cd*, fig. 5, suspended horizontally by a silk thread as spun by the silk-worm, or by a fine silver wire *ab*; on the point of the needle is fixed a small gilt ball made of the pith of elder; and the whole is covered with a glass case to protect it from moisture and currents of air. The pith ball, when the apparatus is at rest, is in contact with the knob *e* of a metallic conductor *fe*, which passes through a hole in the glass case, and is secured in its place by cement; but when an excited body is made to touch the conductor, the pith ball in contact with it is similarly excited, and recedes from it to an extent proportional to the degree of excitement. The needle



Fig. 5.

consequently describes the arc of a circle, which is measured on the graduated arc AB , and in its revolution twists the supporting thread more or less according to the length of the arc described. The torsion thus occasioned calls into play the elasticity of the thread,—a feeble but constant force, which opposes the movement of the needle, measures by the extent to which it is overcome the repulsive force exerted, and brings back the needle to its original position as soon as the electric equilibrium is restored. It has been proved that the force which causes the torsion is exactly proportional to the arc described by the needle.

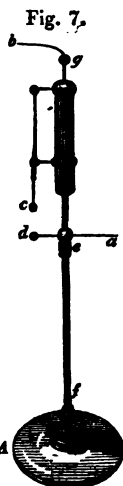
Balance Electrometer.—Harris has made a happy application of the common balance and weights to estimate the mutual attraction of oppositely electrified surfaces. The apparatus, figure 6, consists of a brass beam BB' , supported by a conductor CD standing on a wooden frame AA' ; d is a scale for holding weights, and x its support; a, b , are gilt cones made of light wood, a being suspended by a silver wire from B' , and b insulated by the glass support $A'd'$. The instrument is prepared for use by placing a and d in exact equipoise; the cone a is suspended so that its base shall be opposite and parallel to the base of the cone b , as may be done by means of three adjusting screws in the frame AA' ; and b is raised by help of a graduated brass slide c , until the bases of the cones are just in contact. The cone b is then depressed to any desired distance, which may be varied at will during an experiment; and it is connected with the inner coating of a Leyden jar, the outer coating of which communicates with the frame AA' , and along CD with the cone a : these cones may thus be made parts of a charged Leyden jar, and be oppositely excited, as indicated by the signs $+$ and $-$. The attractive forces exerted between their bases tend to draw down the cone a into contact with b , discharging the jar; but before it can do so, it has to overcome the weight which may be in the scale d . By this ingenious contrivance any number of attractive forces are estimated by a common standard, namely, the number of grains which each is able to raise.

Unit Jar.—This is another contrivance by Harris, and is a most important addition to our stock of electrical apparatus. It is form-

Fig. 6.



ed of a small inverted Leyden jar, figure 7, supported and insulated by a slender glass rod *ef*, which is covered with lac varnish, and fixed into a wooden frame *A*. The inner coating of this jar is in metallic contact with a brass ball *d* and a wire *a*, which wire communicates with the prime conductor of an active electrical machine; whereas the brass ball *c* and wire *b* are connected with its outer coating. If the wire *b* be held in the hand, or otherwise communicate with the ground, the electrical machine being in action, the jar is charged in the usual manner, and is discharged by a spark passing between the two brass balls *c* and *d*. The interval may be increased or diminished by causing one of the balls to be moveable by means of a slide or screw. It will be readily conceived that successive sparks through the same interval must be caused by equal quantities of electricity; and experiment shows this to be the case, provided the apparatus is clean and dry, and the charges are taken nearly at the same time, that is, while the air in relation to temperature, pressure, and moisture, may be considered constant. On taking six successive sparks we employ six times as much electricity as for one charge, and three times as much as for two charges, the quantity of electricity being proportional to the number of charges. It is on this account Harris introduced the term unit jar.



The principal use of the unit jar is in charging other Leyden jars with known proportions of electricity. Thus, if the unit jar be charged by the prime conductor, while its outside communicates through the wire *b* with the inside of a large Leyden jar standing on the ground, the + fluid repelled from the unit jar gives an equal + charge to the inner coating of the large jar, and its outer coating is rendered — by induction. Under these circumstances the effect of a spark between *c* and *d* is merely to neutralize the coatings of the unit jar, without affecting the state of the large jar. On giving a second charge to the unit jar the large jar receives an increment equal to what it received from the first charge, and the second spark merely restores the equilibrium of the unit jar as before. A third and fourth charges of the unit jar act on the same principle; and, by continuing the process, any known proportions may be given. If the opposite coatings of a jar so charged be connected with the cones of the balance electrometer previously de-

scribed, the attractive forces due to known relative quantities of electricity may be precisely determined.

Electric Intensity.—Before concluding this account of electrometers, it will be useful to refer to the kind of information which they supply. From their mode of action, it is plain that they indicate the *degree* of electric excitement, the remoteness from the unexcited state, a condition expressed by the terms *tension* and *intensity*. If two insulated brass disks of equal size be supplied with equal quantities of free electricity, they will affect an electrometer equally, and therefore their intensity or tension is equal; but if one of the disks be larger than the other, the smaller will have the highest tension. In fact, one square inch of the smaller disk will possess more free electricity than the larger, and that is precisely the condition which constitutes differences of intensity. Of any number of electrified substances, that will have the highest intensity which has the most free electric fluid on unity of surface.

LAWS OF ELECTRICAL ACCUMULATION.

1. The quantity of free electricity which an insulated conductor is capable of receiving is independent of its quantity of matter. Thus, two brass spheres of the same size, one solid and the other hollow, will take equal quantities of electricity, and possess equal intensities. The cause of this is referable to the second law.

2. The free electricity of an insulated conductor is always accumulated on its surface, where it forms a layer or stratum enveloping the substance on every side, and therefore possessed of the same figure. Thus, an excited sphere, the surface of which is exactly fitted with two thin metallic hemispheres, loses the whole charge, when, by means of glass handles, the hemispheres are suddenly removed. The cause of free electricity being disposed upon the surface of conductors is ascribed to the mutual repulsion of its particles, which gives them a tendency to recede as far as possible from each other, and to be arrested at the surface solely by some counteracting force, such as the interposition of an imperfect conductor.

3. The mode in which electricity is distributed over the surface of a conductor is dependant on its figure. On a sphere it forms an uniform stratum of equal thickness all around, that is, each part of the surface has the same quantity of electricity as any other part of equal size. But on an ellipsoid the stratum is thickest at the ex-

tremities of the longer axis, and the accumulation at those parts is greater and greater as the length of that axis becomes more and more predominant. In all conductors which are much longer than broad, as in a narrow metallic bar, as also in those which have elongated pointed terminations, the principal accumulation is at the ends and projecting points. The inequality of distribution is just as conspicuous in a negatively as in a positively excited conductor. Coulomb proved these facts experimentally by touching the different parts of electrified conductors by a *proof-plane*, which is a very small disk of gilt paper insulated by a handle of lac resin, and estimating the tension of the proof-plane by his torsion electrometer: he found that this plane always took from the spot touched a constant proportion of the electricity accumulated at that spot, and therefore the relative intensities of the plane, after contact with different parts of an electrified conductor, exactly represented the electric accumulation of the parts so touched. For these and other experiments of Coulomb on electrical actions, the reader may consult Biot's *Traité de Physique*. Harris, in a late essay read at the Royal Society, has shown sources of fallacy in this mode of investigation, of which Coulomb does not seem to have been conscious: how far they affect his principal conclusions remains to be decided.

The unequal accumulation of electricity on conductors is a direct consequence of the law of electric repulsion; and Poisson, assuming the truth of that law, has arrived by calculation at the very same conclusions which Coulomb obtained by experiment. Those who are prepared to follow such very high mathematical inquiries are referred to Poisson's original Essay, to the article on Electricity by Whewell in the *Encyclopedia Metropolitana*, and to a late work on Electricity by Murphy.

4. The electric fluid accumulated at the surface of conductors tends to escape by the repulsion of its particles. Its pressure against the air, or its effort to escape, at any part is considered proportional to the square of the quantity; so that if the electric accumulations at four different parts of an excited conductor are as 1, 2, 3, and 4, the pressure against the air at those parts will be as 1, 4, 9, and 16. Hence electricity passes off with great rapidity from the ends or projecting points of conductors, a result quite conformable to experience. But the equilibrium of an excited conductor is perhaps never entirely restored by the direct

diffusion of its excess due to its own repulsion; for the conductor necessarily tends to induce a state opposite to itself in contiguous conductors and in the circumambient air, and then the attraction of oppositely electrified surfaces is called into play.

5. Coulomb proved experimentally, by aid of his torsion electrometer, that the repulsion of two similarly electrified bodies varies inversely as the square of their distances. If the electric charge on one of them vary, while that on the other and the distance are constant, the repulsion will vary simply as the quantity. Thus, let the free electricity on A be expressed by 4, and that on B by 1, and the distance be always 1 inch, then if the charges on B vary as 1, 2, 3, 4, the repulsion will also vary as 1, 2, 3, 4; for the successive additions to B merely act by augmenting in the same ratio the number of repulsive particles influenced by the constant charge on A. The repulsion in these cases may be denoted by the product of the two charges. For example, when the charges on A and B are 4 and 1, the repulsion will be $4 \times 1 = 4$; when they are 4 and 2, the repulsion is $4 \times 2 = 8$, or twice 4; when 4 and 3, it is $4 \times 3 = 12$, or three times four; and when 4 and 4, the repulsion is $4 \times 4 = 16$, or four times four. If in the last case the charge on B fall to 2, the repulsion becomes $4 \times 2 = 8$, as before; and then should the charge on A be also reduced to 2, the repulsion will be $2 \times 2 = 4$. Hence when the *whole* quantity of electricity changes, the repulsion varies as the square of the quantity.

6. The attraction of two oppositely electrified bodies varies inversely as the square of the distance between them. Coulomb, who verified this law by experiment, also showed that the attractive force, the distance being constant, varies by the same law as that for repulsion just stated. If A and B are equally and oppositely excited, so that we may represent the free electricity on each by 4, and their mutual attraction by $4 \times 4 = 16$, then if the quantity on B successively become 3, 2, and 1, the corresponding attractions will be 12, 8, 4; and should the quantity on A and on B vary together, so as to be reduced on both from 4 to 2, and from 2 to 1, the attractions will be 16, 4, and 1. Thus, when the *whole* quantity of electricity changes, the attraction varies as the square of the quantity.

Harris has given a beautiful demonstration of these laws by means of his balance electrometer and unit jar (pages 129, 130),

the cones *a*, *b*, of figure 6, being connected respectively with the outer and inner coatings of a large Leyden jar. On giving to it a constant charge by means of the unit jar, and varying the distance, the weights raised, or the attractive force, were found to vary inversely as the square of the distance between the cones. On preserving the distance constant, giving a charge capable of raising one grain, and then successively doubling, trebling, and quadrupling the quantity first given to the inner coating, the weights raised were 4, 9, and 16 grains. This strictly conforms with the foregoing statement; for on doubling the charge to the inner coating of the Leyden jar, the electricity on the cone *b*, connected with it, is also doubled, and the double charge on *b* doubles the induced charge on *a*. Hence the quantity on both cones being doubled, the force ought to be quadrupled.

7. It may be inferred from the law No. 6, that when, in two oppositely excited bodies, the whole quantity of electricity and the distance vary together and at the same rate, the attractive force will be unchanged. This has been fully proved by Harris. On putting 5 grains into his balance, giving a charge sufficient to raise that weight at a certain distance, and then successively doubling, trebling, and quadrupling that distance, it will be necessary, in order to raise the 5 grains, to give a double, treble, and quadruple charge to the inner coating of the Leyden jar communicating with cone *b*. In fact, doubling the electricity on both cones, is to quadruple the attractive force between them; and doubling the distance, diminishes the force by four times: the force is thus diminished by one cause as much as it is increased by the other, and therefore continues unchanged.

Harris has demonstrated the same law by observing the *striking distance* of a charged jar, that is, the interval through which the electricity will pass so as to discharge it. For this purpose the inner and outer coating are separately connected with a conductor terminating in a brass ball, one of which is attached to a graduated slide, so as to be fixed at any required distance from the other ball. On causing the distances between the balls to vary in the ratio of 1, 2, 3, 4, the jar will discharge itself by the passage of a spark, when the charge on each coating is increased in the same ratio. The obstacle which the electricity has to overcome before it can discharge the jar, is the interposed air; and that obstacle may be regarded as constant in experiments performed

at the same time, since it is found to depend on the density of the air.

8. Harris ascertained the nature of the influence exerted by the atmosphere over the striking distance of a charged Leyden jar, by including the balls connected with its outer and inner coating within glass vessels susceptible of exhaustion. He then found that the resistance to the passage of a charge varies as the square of the density of the air. Thus, when the density was made to vary in the ratio of 1, 2, 4, the charge passed through a constant interval when the quantity added to the inner coating varied in the same ratio. Now, when the charges were as 1, 2, 4, the attractive forces, by law No. 6, were as 1, 4, 16, which represent the corresponding obstacles caused by the air. Agreeably to the same law, the striking distance, when the charge is constant, varies inversely as the density of the air: a charge which strikes through one inch of air when the barometer is at 30 inches, will pass through two inches in air so rarefied as to support only 15 inches of mercury, and through four inches when the mercurial column is 7.5 inches. Hence in a perfect vacuum a Leyden jar ought to discharge itself through any interval; and in the higher parts of the atmosphere, where the air is much rarefied, two oppositely-excited clouds will neutralize each other, though separated by very great distances.

It is not apparent from the preceding remarks, whether the striking distance is influenced by change of the density or the elasticity of the confined air, since in rarefying air by the air-pump, the rarefaction increases, and the elasticity decreases at the same rate. Harris has shown, contrary to what one might anticipate, that the influential condition is density, and not elasticity. For on rarefying air by heat so as to preserve its original elasticity, the striking distance was exactly the same as in cold air rarefied to the same degree by the air-pump; and in air first rarefied by the air-pump, and then heated until it had recovered its original elasticity, its volume and density being kept the same, the varied elasticity had no influence on the charge required to pass through a constant distance. From these and similar experiments Harris infers that the remarkable conducting power known to be possessed by hot air is due to its rarity alone.—Though I have not had occasion to repeat these experiments on hot air, I have entire confidence in their accuracy; inasmuch as, not to mention the known

skill and exactness of Harris, I find that the striking distance for the same charge is greater in air than in carbonic acid gas, and greater in hydrogen gas than in air, the elasticities being equal.

9. The continuance of an excited charge on an insulated conductor is commonly ascribed to the pressure of the air. An opposite opinion, however, has been maintained. Morgan (Phil. Trans. 1785) published some experiments to prove that a space entirely free from air, such as a Torricellian vacuum, is a non-conductor of electricity; and Cavallo (Treatise on Electricity) showed that exhaustion may be carried very far within the bell-jar of an air-pump without an electrified body placed under it losing its charge. On repeating these experiments, at the request of Harris, I obtained similar results. A slip of gold leaf diverging at an angle of 60° , continued so for hours in air expanded 100 times; and in air rarefied 300 times, a feeble charge was retained for a whole week. The loss observed in still further states of exhaustion, may be ascribed to the excited body inducing an opposite state in the conducting materials of the air-pump, thereby calling into activity a force which co-operates with the repulsion of its own particles. The preceding phenomena appear to indicate the existence of an adhesive force between the particles of electricity and the surface of bodies, which causes an obstacle to their escape.

10. Some elegant and most ingenious experiments have been made by Wheatstone to determine the velocity of electricity (Phil. Trans. 1834). His principal conclusions are the following:—

1. The velocity of electricity along a copper wire exceeds that of light through the planetary space.

2. The disturbance of the electric equilibrium in a wire communicating at its extremities with the two coatings of a charged jar, travels with equal velocity from the two ends of the wire, and occurs latest in the middle of the circuit.

3. The light of electricity of high tension has a less duration in passing as a spark than the millionth part of a second.

HISTORICAL NOTICE.

The science of electricity is of modern origin. The knowledge of the ancients was confined to the fact that amber and the *lyncurium* (supposed to be tourmalin) acquired the property of attracting light bodies by friction. It was not known that other bodies

may be similarly excited until the commencement of the 17th century, when Gilbert of Colchester detected the same property in a variety of other substances, and thereby laid the foundation of the science of electricity. A few additional facts were noticed during the same century by Boyle, Otto de Guericke, and Wall, and in 1709 Hawkesbee published an account of many curious electrical experiments; but no material progress was made until Stephen Grey (Phil. Trans. 1729 to 1733) drew the distinction between conductors and non-conductors of electricity, and illustrated it by new and striking experiments. Soon after, Dufay in France distinguished between the two kinds of electricity; and in 1759 (Phil. Trans. li. 340) Symmer added the important fact that friction develops both kinds of electricity at the same time, an observation which led to the theory of two electric fluids as now understood. These discoveries, added to the confirmation of Franklin's opinion as to the identity of the cause of lightning and electricity, fixed the attention of scientific men upon the new study, and soon acquired for it a high rank among the sciences.

For further details respecting its origin and early progress the reader may consult the history of electricity by Priestley.

SECTION IV.

GALVANISM.

THE science of Galvanism owes its name and origin to the experiments on animal irritability made by Galvani, Professor of Anatomy at Bologna, in the year 1790. In the course of the investigation he discovered the fact, that muscular contractions are excited in the leg of a frog recently killed, when two metals, such as zinc and silver, one of which touches the crural nerve, and the other the muscles to which it is distributed, are brought into contact with one another. Galvani imagined that the phenomena are owing to electricity present in the muscles, and that the metals only serve the purpose of a conductor. He conceived that the animal electricity originates in the brain, is distributed to every part of the system, and resides particularly in the muscles. He was of opinion that the different parts of each muscular fibril are in opposite states of electrical excitement, like the two surfaces of a charged Leyden phial, and that contractions take place whenever

the electric equilibrium is restored. This he supposed to be effected during life through the medium of the nerves, and to have been produced in his experiments by the intervention of metallic conductors.

The views of Galvani had several opponents, one of whom, the celebrated Volta, Professor of Natural Philosophy at Pavia, succeeded in pointing out their fallacy. Volta maintained that electric excitement is due solely to the metals, and that the muscular contractions are occasioned by the electricity thus developed passing along the nerves and muscles of the animal. To the experiments instituted by Volta we are indebted for the first voltaic apparatus, which has properly received the name of the *voltaic pile*; and to the same distinguished philosopher belongs the real merit of laying the foundation of the science of Galvanism (Phil. Trans. 1800).

The identity of the agent concerned in the phenomena of galvanism and of the common electrical machine, is now a matter of demonstration. Voltaic and common electricity are due to the same force, excited by different conditions, operating in general in a different manner and under different circumstances. The effects of the latter are caused by a comparatively small quantity of electricity brought into a state of insulation, in which state it exerts a high intensity, as evinced by its remarkable attractive and repulsive energies, and by its power to force a passage through obstructing media. In galvanism the electric agent is more intimately associated with other substances, is developed in large quantity, but never attains a high tension, and produces its peculiar effects while flowing along conductors in a continuous current.

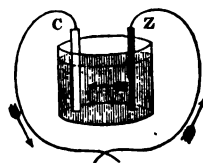
VOLTAIC ARRANGEMENTS OR CIRCLES.

Arrangements for exciting galvanism are divided into simple and compound; the former being voltaic circles in their most elementary form, and the latter a collection of simple circles acting together: it will hence be proper to commence the description of them with the most simple.

Simple Voltaic Circles.—When a plate of zinc and a plate of copper are placed in a vessel of water, and the two metals are made to touch each other, either directly or by the intervention of a metallic wire, galvanism is excited. The action is, indeed, very

feeble, and not to be detected by ordinary methods ; but if a little sulphuric acid be added to the water, numerous globules of hydrogen gas will be evolved at the surface of the copper. This phenomenon continues uninterruptedly while metallic contact between the plates continues, in which state the circuit is said to be *closed*; but it ceases when the circuit is broken, that is, when metallic contact is interrupted. The hydrogen gas which arises from the copper plate results from water decomposed by the electric current, and its ceasing to appear indicates the moment when the current ceases. In this case the voltaic circle consists of zinc, copper, and interposed dilute acid ; and the circle gives rise to a current only when the two metals are in contact. This arrangement is shown in figure 1,

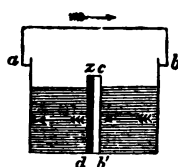
Fig. 1.



where metallic contact is readily made or broken by means of copper wires soldered to the plates. By employing a galvanometer (p. 158), it is found that a current of + electricity continually circulates in the closed circuit from the zinc through the liquid to the copper, and from the copper along the conducting wires to the zinc, as indicated by the arrows in the figure. A current of - electricity, agreeably to the theory of two electric fluids, ought to traverse the apparatus in a direction precisely reversed ; but for the sake of simplicity I shall hereafter indicate the course of the + current only.

It matters not, so far as voltaic action is concerned, at what part the plates of fig. 1 touch each other. A current takes place, whether contact between the plates is made below where covered with liquid, above where uncovered, or along the whole length of the plates, provided both plates are immersed in the same vessel of dilute acid. Immersion of one plate only in the acid solution, however contact between the plates may be made, does not excite voltaic action ; nor does it suffice to have one plate in one vessel, and the other plate in another vessel. A plate of zinc soldered to

Fig. 2.



one of copper, and plunged into dilute acid, gives a current passing from the zinc through the fluid round to the copper ; but if the soldered plates are cemented into a box with a wooden bottom and metallic sides, so as to form two *separate* cells, as shown in a vertical section by figure 2, then the introduction of dilute acid to the cells will not excite a current, unless the fluid of the

cells be made to communicate by means of moistened fibres of twine, cotton, or some porous matter, or, as in the figure, by wires, *a b*, soldered to the metallic sides which contain the dilute acid, or dipping into the acid itself. Then the positive current circulates in the direction shown by the arrows.

Instead of a pair of plates being soldered together, they may be connected by a wire, and plunged into separate cells, *a e*, *b e*, figure 3, in which *d e* acts as a partition, provided the + current issuing from the zinc plate, *z*, is conveyed by a wire, *f g h i*, or some conducting medium, into the cell, *b e*, in which the copper plate, *c*, is immersed.



Fig. 3.

A simple voltaic circle may be formed of one metal and two liquids, provided the liquids are such that a stronger chemical action is induced on one side than on the other. Thus, on cementing a plate of zinc, *z*, into a box, figure 4, and putting a solution of salt into the cell, *b b'*, and dilute nitric acid into the cell, *a a'*, a + current will be excited in the direction of the arrows, provided the circuit be completed by a wire, *a b*, attached to the metallic sides of the box, or dip into the liquid of the cells.



Fig. 4.

Nay, the same acid solution may occupy both cells, provided some condition be introduced which shall cause one side of the zinc to be more rapidly dissolved than the other; as by the plate being rough on one side and polished on the other, or by the acid of one cell differing from that of the other either in strength or temperature. So general is this principle, that a single lamina of copper immersed in a tube of dilute acid will give rise to a current, provided the acid at one end of the tube is stronger than that at the other: the copper being unequally acted on at its different parts, the result is the same as when two different liquids are used.

An interesting kind of simple voltaic circle is afforded by commercial zinc. This metal, as sold in the shops, contains traces of tin and lead, with rather more than one per cent. of iron, which is mechanically diffused through its substance: on immersion in dilute sulphuric acid, these small particles of iron and the adjacent zinc form numerous voltaic circles, transmitting their currents through the acid which moistens them, and disengaging a large quantity of hydrogen gas. Pure distilled zinc is very slowly acted on by dilute sulphuric acid of sp. gr. ranging from 1.068 to 1.215; but if fused

with about 2 per cent, or rather less, of iron filings, it is as readily dissolved as commercial zinc. In like manner, pure iron or steel is less readily acted on by dilute sulphuric acid than the same substances after fusion with small quantities of platinum or silver. Sturgeon has remarked that commercial zinc, with its surface amalgamated, which may be done by dipping a zinc plate into nitric acid diluted with two or three parts of water, and then rubbing it with mercury, resists the action of dilute acid fully as well as the purest zinc. This fact, of which Faraday in his late researches has made excellent use, appears due to the mercury bringing the surface of the zinc to a state of perfect uniformity, preventing those differences between one spot and another, which are essential to the production of minute currents; one part has the same tendency to combine with electricity as another, and cannot act as a discharger to it (Faraday).

While the current formed by the contact of two metals gives increased effect to the affinity of one of them for some element of the solution, the ability of the other metal to undergo the same change is proportionally diminished. Thus, when plates of zinc and copper touch each other in dilute acid, the zinc oxidizes more, and the copper less, rapidly than without contact. This principle was beautifully exemplified by the attempt of Davy to preserve the copper sheathing of ships. A sheet of copper immersed in sea-water, or a solution of chloride of sodium, in an open vessel, undergoes rapid corrosion; and a green powder commonly termed submuriate of copper, but which is really an oxy-chloride, is generated: atmospheric oxygen dissolved in sea-water unites both with copper and sodium, the latter yields its chlorine to another portion of copper, and the oxide and chloride of copper unite. But if the copper be in contact with zinc or some metal more electro-positive than itself, the zinc undergoes the same change as the copper did, and the latter is preserved. Davy found that the quantity of zinc required thus to form an efficient voltaic circle with copper was very small. A piece of zinc as large as a pea, or the head of a small round nail, was found fully adequate to preserve 40 or 50 square inches of copper; and this wherever it was placed, whether at the top, bottom, or middle of the sheet of copper, or under whatever form it was used. And when the connexion between different pieces of copper was completed by wires, or thin filaments of the 40th or 50th of an inch in diameter, the effect was the same;

every side, every surface, every particle of the copper remained bright, whilst the iron or the zinc was slowly corroded. Sheets of copper defended by 1-40th to 1-1000th part of their surface of zinc, malleable and cast iron, were exposed during many weeks to the flow of the tide in Portsmouth harbour, and their weight ascertained before and after the experiment. When the metallic protector was from 1-40th to 1-150th, there was no corrosion nor decay of the copper; with smaller quantities, such as 1-200th to 1-460th, the copper underwent a loss of weight which was greater in proportion as the protector was smaller; and as a proof of the universality of the principle, it was found that even 1-1000th part of cast iron saved a certain proportion of the copper (Phil. Trans. 1824).

Unhappily for the application of this principle in practice, it is found that unless a certain degree of corrosion takes place in the copper, its surface becomes foul from the adhesion of seaweeds and shell-fish. The oxy-chloride of copper, formed when the sheathing is unprotected, is probably injurious to these plants and animals, and thus preserves the copper free from foreign bodies.

Simple voltaic circles may be formed of very various materials; but the combinations usually employed consist either of two perfect and one imperfect conductor of electricity, or of one perfect and two imperfect conductors. The substances included under the title of perfect conductors are metals and charcoal, and the imperfect conductors are water and aqueous solutions. It is essential to the operation of the first kind of circle, that the imperfect conductor act chemically on one of the metals; and in case of its attacking both, the action must be greater on one metal than on the other. It is also found generally, if not universally, that the metal most oxidized is positive with respect to the other, or bears to it the same relation as zinc to copper in figures 1, 2, and 3. Davy, in his Bakerian lecture for 1826 (Phil. Trans.), gave the following list of the first kind of arrangements, the imperfect conductor being either the common acids, alkaline solutions, or solution of metallic sulphurets, such as sulphuret of potassium. The metal first mentioned is positive to those standing after it in the series.

With common acids.—Potassium and its amalgams, barium and its amalgams, amalgam of zinc, zinc, cadmium, tin, iron, bismuth,

antimony, lead, copper, silver, palladium, tellurium, gold, charcoal, platinum, iridium, rhodium.

With alkaline solutions.—The alkaligenous metals and their amalgams, zinc, tin, lead, copper, iron, silver, palladium, gold, and platinum.

With solutions of metallic sulphurets.—Zinc, tin, copper, iron, bismuth, silver, platinum, palladium, gold, charcoal.

Faraday has shown that the presence of water is not essential. A battery may be composed of other liquid compounds, such as a fused metallic chloride, iodide, or fluoride, provided it is decomposable by galvanism, and acts chemically on one metal of the circle more powerfully than on the other.

The following table of voltaic circles of the second kind is from Davy's Elements of Chemical Philosophy:—

Solution of Sulphuret of Potassium Potassa Soda	Copper Silver Lead Tin Zinc Other Metals Charcoal	Nitric Acid Sulphuric Acid Hydrochloric Acid Any solutions containing Acid.
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The most energetic of these combinations is that in which the metal is chemically attacked on one side by sulphuret of potassium, and on the other by an acid. The experiment may be made by pouring dilute nitric acid into a cup of copper or silver, which stands in another vessel containing sulphuret of potassium. The following arrangements may also be employed:—Let two pieces of thick flannel be moistened, one with dilute acid and the other with the sulphuret, and then placed on opposite sides of a plate of copper, completing the circuit by touching each piece of flannel with a conducting wire: or, take two discs of copper, each with its appropriate wire, immerse one disc into a glass filled with dilute acid, and the other into a separate glass with alkaline solution, and connect the two vessels by a few threads of amianthus or cotton moistened with a solution of salt. A similar combination may be disposed in this order:—Let one disc of copper be placed on a piece of glass or dry wood; on its upper surface lay in succession three pieces of flannel, the first moistened with dilute acid, the second with solution of salt, and the third with sulphuret of potassium, and then cover the last with the other disc of copper.

Metallic bodies are not essential to the production of galvanic phenomena. Combinations have been made with layers of charcoal and plumbago, of slices of muscle and brain, and beet-root and wood; but the force of these circles, though accumulated by the union of numerous pairs, is extremely feeble, and they are very rarely employed in practice.

Of the simple voltaic circles above described, the only one used for ordinary purposes is that composed of a pair of zinc and copper plates excited by an acid solution arranged as in figure 1. The form and size of the apparatus are exceedingly various. Instead of actually immersing the plates in the solution, a piece of moistened cloth may be placed between them. Sometimes the copper plate is made into a cup for containing the liquid, and the zinc is fixed between its two sides, as shown by the accompanying transverse vertical section, figure 5; care being taken to avoid actual contact between the plates, by interposing pieces of wood, cork, or other imperfect conductor of electricity. Another contrivance, which is much more convenient, because the zinc may be removed at will and have its surface cleaned, is that represented by the annexed woodcut (fig. 6). C is a cup made with two cylinders of sheet copper, of unequal size, placed one within the other, and soldered together at bottom, so as to leave an intermediate space *a a*, for containing the zinc cylinder *z* and the acid solution. The small copper cups *b b* are useful appendages; for by filling them with mercury, and inserting the ends of a wire, the voltaic circuit may be closed or broken with ease and expedition. This apparatus is very serviceable in experiments on electro-magnetism.

Another kind of circle may be formed by coiling a sheet of zinc and copper round each other, so that each surface of the zinc may be opposed to one of copper, and separated from it by a small interval. The London Institution possesses a very large apparatus of this sort, made under the direction of Pepys, each plate of which is 60 feet long and two wide. The plates are prevented from coming into actual contact by interposed ropes of horsehair; and the coil, when

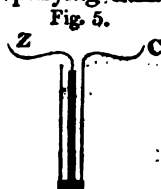


Fig. 5.

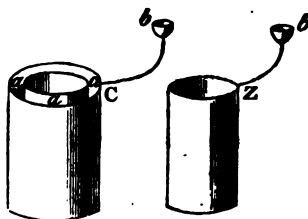
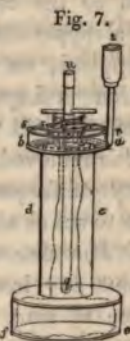


Fig. 6.

used, is lifted by ropes and pulleys, and let down into a tube containing dilute acid. The contrivance of opposing one large connected surface of zinc to a similar surface of copper originated with Hare of Philadelphia, who, from its surprising power of igniting metals, gave it the name of *calorimotor*.

An excellent arrangement has been described by Daniell, of which fig. 7 represents a modification more simple and perhaps equally effective. It consists of a cylinder of copper, *abcdef*, 3 inches wide from *a* to *b*, $1\frac{1}{2}$ inches from *c* to *d*, and 4 inches from *e* to *f*, the corresponding heights being half an inch, 5 inches, and 2 inches; *lmno*, is a collar of copper, which by the arms *r r*, *s s*, rests on the top of the cylinder, and to which a membranous tube formed of the gullet of an ox is tied, the membrane being longer than the copper cylinder so as to be baggy below and nearly fill the space *ef*; *u p q*, is a rod of amalgamated zinc resting on the collar *lmno*, by means of a piece of wood *r s*, which perforates it; *u*, *t*, are cups to hold mercury for making contact. Between the membrane and copper cylinder is poured a saturated solution of blue vitriol, and within the membrane dilute sulphuric acid of about sp. gr. 1.136, which is made with 1 measure of strong acid and 8 of water. The exciting acid is thus in contact with the zinc, but not with the copper. When this circle is in action, the electric current passes from the zinc through the acid, membrane, and solution of blue vitriol to the copper. The arrangement is founded on two important principles, established by Daniell:—



1. However active a circle, as made heretofore, may be when first excited, its energy is known rapidly to diminish, and in a few minutes to fall much below its original power. Daniell has traced the cause to reduction of oxide of zinc by nascent hydrogen at the surface of the copper plate, whereby this metal becomes coated with zinc, and is thus more or less converted at its surface into a zinc plate; and as two zinc plates under like conditions do not produce a current, of course the action declines. In the new circle this defect is avoided by the membranous septum which protects the copper plate from contact with the solution of zinc: the nascent hydrogen reduces oxide of copper, and a film of bright copper is

deposited on the copper plate, thus constantly presenting a clean good conducting surface; while the hydrogen itself, not escaping as gas, no longer opposes an obstacle, as it does when allowed to assume the gaseous form, to the passage of electricity from the solution to the copper plate. To supply the loss of oxide of copper, a copper disc, *a, v, x, b*, studded with holes like a cullender, is supplied, on which rest crystals of blue vitriol, whereby the solution is kept saturated and its conducting power preserved. When the acid within the membrane is exhausted, the membrane itself is removed, and fresh acid supplied; but to prevent the necessity of frequent renewal, the lower part of the membrane is made to act as a reservoir of acid.

2. The zinc of a pair of plates may be much reduced in size without any loss of power: strong chemical action on a small surface of zinc, a good conducting solution, and a bright large surface of copper, are conditions by which a powerful action is ensured. This is indicated by Davy's protectors for copper sheathing (page 141); but it was not previously known that the principle was applicable to the construction of voltaic apparatus. The great merit of this circle is its *constancy*: by keeping up the supply of blue vitriol and acid, its energy will continue invariable for hours, or for an indefinite period. A similar apparatus has been described by Mullins (*Phil. Mag. & An.* ix. 122).

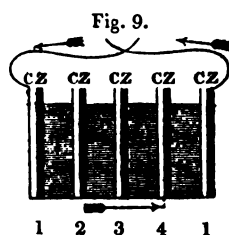
Compound voltaic circles.—This expression is applied to voltaic arrangements which consist of a series of simple circles. The first combinations of the kind were described by Volta, and are now well known under the names of *voltaic pile* and *crown of cups*. The voltaic pile is made by placing pairs of zinc and copper, or zinc and silver plates, one above the other, as in figure 8, each pair being separated from those adjoining by pieces of cloth, rather smaller than the plates, and moistened with a saturated solution of salt. The relative position of the metals in each pair must be the same in the whole series; that is, if the zinc be placed below the copper in the first pair, the same order should be observed in all the others. Without such precaution the apparatus would give rise to opposite currents, which would neutralize each other more or less according to their relative forces. The pile, which may consist of any convenient number of combinations, should be contained in a frame

Fig. 8.

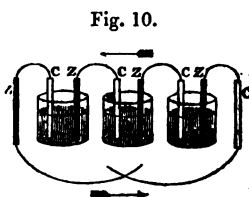


formed of glass pillars fixed into a piece of thick dry wood, by which it is both supported and insulated. Any number of these piles may be made to act in concert by establishing metallic communication between the + extremity of each pile and the - extremity of the pile immediately following.

The voltaic pile is now rarely employed, because we possess other modes of forming galvanic combinations which are far more powerful and convenient. The galvanic battery proposed by **Crnickshank** consists of a trough of baked wood, about 30 inches long, in which are placed at equal distances 50 pairs of zinc and copper plates previously soldered together, and so arranged that the same metal shall always be on the same side. Each pair is fixed in a groove cut in the sides and bottom of the box, the points of junction being made water-tight by cement. The apparatus thus constructed is always ready for use, and is brought into action by filling the cells left between the pairs of plates with some convenient solution, which serves the same purpose as the moistened cloth in the pile of Volta. By means of the accompanying woodcut the mode in which the plates are arranged will easily be understood.

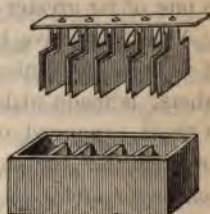


Other modes of combination are now in use, which facilitate the employment of the voltaic apparatus and increase its energy. Most of these may be regarded as modifications of the crown of cups. In this apparatus the exciting solution is contained in separate cups or glasses, disposed circularly or in a line; each glass contains a pair of plates; and each zinc plate is attached to the copper of the next pair by a metallic wire, as represented in figure 10. Instead of glasses, it is more convenient in practice to employ a trough of baked wood or glazed earthenware, divided into separate cells by partitions of the same material; and in order that the plates may be immersed into and taken out of the liquid conveniently and at the same moment, they are all attached to a bar of dry wood, the necessary connexion between the zinc of one cell and the copper of the adjoining one being accomplished, as in figure 11, by a slip or wire of copper.



A material improvement in the foregoing apparatus was suggested by Wollaston (Children's Essay in Phil. Trans. 1815), who recommended that each cell should contain one zinc and two copper plates, so that both surfaces of the former metal might be opposed to one of the latter. The plates communicate with each other, and the zinc between them with the copper of the adjoining cell. An increase of one-half the power is said to be obtained by this method.

Fig. 11.



A variation of this contrivance was suggested by Hart of Glasgow, who proposed to have the double copper plates of the preceding battery made with sides and bottoms, so that, as in figure 5, they may contain the exciting liquid. The plates are attached, as in figure 11, to a bar of wood, and supported above the ground by vertical columns of the same material, by which they are insulated. The cells are filled by dipping the whole battery into a trough of the same form, full of the exciting liquid. (Brewster's Journal, iv. 19.)

The size and number of the plates may be varied at pleasure. The largest battery ever made is that by Children, above referred to, the plates of which were six feet long, and two feet eight inches broad. The common and most convenient size for the plates is four or six inches square; and when great power is required, a number of different batteries are united by establishing metallic communication between the + extremity or pole of one battery and the - pole of the adjoining one. A very effective battery was described by Hare under the name of the *deflagrator*, which consisted of 80 zinc plates, 9 inches by 6 in size, and 80 copper plates, 14 inches by 6, coiled together, and so connected that the whole could be immersed into the exciting liquid, or removed from it, at the same instant (An. of Phil. xvii. 329). The great battery of the Royal Institution, with which Davy made his celebrated discovery of the compound nature of the alkalis, was composed of 2000 pairs of plates, each plate having 32 square inches of surface. It is now recognized, however, that such large compound batteries are by no means necessary. Increasing the number of plates beyond a very moderate limit gives for most purposes no proportionate increase of power; so that a battery of 50 or 100

pair of plates, thrown into vigorous action, will be just as effective as one of far greater extent.

A very effective battery, which, I apprehend, from its constancy of action, convenience, cheapness, and power will supersede all others, is made with Daniell's simple circles (page 145). Twenty of these, arranged on a wooden tray in two rows, has an energy sufficient for the performance of most experiments of demonstration or research.

The electrical condition of compound voltaic arrangements is similar to that of the simple circle. In the broken circuit no electric current can be traced; but in the closed circuit, that is, when the wires from the opposite ends of the battery are in contact, the galvanometer indicates a positive electric current through the battery itself and along the wires, as shown by the arrows in figures 9 and 10. The direction of the current appears at first view to be different from that of the simple circle; since in the latter the + electric current flows from the zinc through the liquid to the copper, while in the compound circle its direction is from the extreme copper through the battery to the extreme zinc plate. This apparent difference arises from the compound circle being usually terminated by two superfluous plates. The extreme copper and extreme zinc plate of figure 8 are not in contact with the exciting fluid, and therefore contribute nothing to the galvanic action: removing these superfluous plates, which are solely conductors, there will remain four simple circles, namely, the 3 pair of soldered plates marked 2, 3, 4, which act as in figure 2, and the then extreme plates, 1, 1, which are related to each other as the plates in fig. 1. When thus arranged, the direction of the current will be seen to correspond with that of the simple circle.

During the action of a simple circle, as of zinc and copper, excited by dilute sulphuric acid, all the hydrogen developed in the voltaic process is evolved at the surface of the copper. This fact is not apparent when common zinc plates are used, owing to the numerous currents which form on the surface of the zinc (page 141); but when a plate of amalgamated zinc and another of platinum are introduced into dilute sulphuric acid of sp. gr. 1.068, no gas whatever appears until contact between the plates is made, and then hydrogen gas rises solely from the platinum, while zinc is tranquilly dissolved. On weighing the amalgamated plate before and after the action has continued for half an hour or an hour, and

collecting the hydrogen gas evolved during that interval, the weight of the hydrogen set free and of zinc dissolved will be as 1 to 32.3, being the ratio of their chemical equivalents. Faraday, who has proved this, has also shown that in a compound voltaic circle, say of 10 amalgamated zinc plates and 10 of platinum, each of the former during a given period of action loses exactly the same weight, and from each of the latter an equivalent quantity of hydrogen gas is evolved. This separation of one ingredient of the exciting solution at one plate, while the element previously combined with it unites with the other plate, seems essential to voltaic action. It is in some way connected with the passage of the current across the exciting liquid. Oxygen in a free state may by oxidizing zinc cause electric excitement; but the voltaic current is not established unless the oxygen formed part of a previous liquid compound in contact or communication with both the plates.

Among the different kinds of voltaic apparatus is usually placed the electric column of De Luc, which is formed of successive pairs of silver and zinc, or silver and Dutch-metal leaf, separated by pieces of paper, arranged as in a voltaic pile. It is remarkable for its power of exhibiting attractions and repulsions like common electricity, but cannot produce chemical decomposition or any of the effects most characteristic of a voltaic current, and is rather an electrical than a voltaic instrument. It is quoted as a proof of electric developement by contact, since it will continue in action for years without being cleaned or taken to pieces. True it is that the more oxidable metal of the column is slowly corroded, and that no electricity is excited when the paper is quite or nearly free from hygrometric moisture, the presence of which is necessary to the oxidation of the zinc and copper; but at the same time the quantity of electricity excited seems so disproportioned to the corrosion, that the one can scarcely be assigned as the cause of the other.

LAWS OF THE ACTION OF VOLTAIC CIRCLES.

Electricians distinguish between *quantity* and *intensity* in galvanism, as in ordinary electricity (page 131); and by most persons, as also in this work, the same meaning is attached to them. The electric intensity of a voltaic circle is most correctly estimated by the divergence which in the broken circuit it causes

in a gold leaf or other electrometer; and as the intensity is never considerable, it is often necessary to employ a condenser. The experiment is best made by causing a wire attached to one extremity of the circle to touch the condenser, while a wire from its opposite end communicates with the ground. The charges accumulated on the extreme plates of a voltaic circle cannot acquire a high tension, because the liquid which separates them is a good conductor for all charges except such as are of very feeble intensity. Were the opposite ends of a battery to be thrown by any means into opposite electric states, they would retain such charges only as had not intensity enough to force their way across the liquid within its cells. This discharge happens more or less readily, according as the liquid is a better or worse conductor, or its stratum thinner or thicker. Accordingly, a simple circle has necessarily a very feeble tension: if the plates are far asunder, and water or a similar feeble conductor occupy the interval, the quantity of electricity evolved is too small to give any other than a feeble charge; and if the plates are near together, and excited by an acid solution, the electricity, when once arrived at the opposite plates, finds a ready discharge through the solution. The circle which gives the highest tension is one which excites electricity sufficient for duly charging the apparatus, while it opposes an obstacle to spontaneous discharge. A battery of numerous small plates excited by water, or a weak saline or acid solution, fulfils these conditions. The electric current in a closed circuit is said to have a greater or smaller intensity, according to the intensity possessed by the apparatus, when the circuit is broken: the higher its intensity, the more readily will its current force its way through imperfect conductors.

The quantity of electricity circulating in a voltaic battery is exactly the same in all its parts,—along the conducting wires, through any liquid or other conductor with which those wires communicate, and through each of its cells. It is found to be exactly proportional to the magnetic and chemical effects which it is capable of producing; and hence the quantity of electricity moving through any closed circuit is readily estimated either by the deflection which it causes on a magnetic needle, or by its power of chemical decomposition. The quantity of electricity which a circle can set in motion in a given time, depends on the amount and nature of chemical action going on upon its plates.

When quantity of electricity is alone desired, a single pair of plates is just as useful as a compound circle.

The following numerical results were obtained by Ritchie by means of a magnetic galvanometer:—

1. The power of a single pair of plates in deflecting the magnetic needle is directly proportional to the surface of the plates which is covered with dilute acid; that is, if a given deflection is caused by covering one square inch of each plate with liquid, the deflection will be doubled when two square inches are immersed.

2. A plate of zinc introduced into a rectangular cup of copper, as in figure 5, page 144, deflects the needle twice as much as when one side of the zinc and the adjacent surface of copper are protected by a coating of cement from the action of the acid solution.—The varying conditions of the experiments were calculated to affect the quantity of electricity set in motion without changing the intensity; and therefore the results, proving the deflection to depend on quantity and not on tension, entirely conform to general experience.

3. The deflection produced by a pair of plates, in an acid solution of uniform strength, varies inversely as the square root of the distance between them,—a law previously established by Cumming. Thus, if a plate of zinc be placed successively at 1, 4, and 9 inches from a plate of copper, the deflecting powers will be in the ratio of 3, 2, and 1; that is, only twice as great at one inch as at four, and only three times as great at one inch as at nine inches.

4. The same law, as previously deduced by Cumming and Barlow, applies to variations in the length of the wire by which the zinc and copper plates are connected. If, all other circumstances being uniform, the conducting wire varies from 4 feet to 1 foot in length, the deflecting power will vary in the ratio of 1 to 2. Ritchie informs me that with short metallic wires the deflection varies inversely as the square root of the length of the whole circuit, that is, of the solid and liquid conductors taken together. The wire in these experiments must be single, and not coiled as in the multiplier of Schweigger: large wires should be used capable of freely conveying all the electricity which is developed.

Ritchie has also shown, agreeably to general observation, that the deflecting power of a compound circle is not increased by in-

creasing the number of its plates. A single pair of plates with a good conducting liquid within the cell, and supplied with large conducting wires capable of carrying off the whole quantity of electricity set in motion, deflects the needle nearly or quite as much as a battery composed of several pairs of plates of the same size. This is another proof that the direct influence of a number of plates is to increase the intensity and not the quantity of electricity; for the prevailing opinion that the magnetic needle takes no cognizance of intensity is fully borne out by the experiments of Faraday.

Though the quantity of a compound decomposed by a battery is proportional to the actual quantity of electricity which passes, yet, as a compound exposed to voltaic action is almost always an imperfect conductor, the quantity of electricity capable of passing through it varies with its intensity. Hence chemical decomposition depends on quantity and intensity together, and affords a criterion of the increased tension of a compound circle due to an increase in the number of its plates. The quantity of hydrogen gas evolved from water by a battery in a given time, does not vary in the simple ratio of the number of the plates; that is, the gas is not doubled when the number of plates is doubled: the effect increases at a slower rate. Ritchie considers the ratio to be as the square root of the number of plates; so that when the number varies as 1 to 4, the gas evolved is as 1 to 2.

EFFECTS OF GALVANISM.

The effects producible by voltaic combinations are conveniently divisible into the electrical, magnetic, and chemical phenomena.

I. *Electrical Effects.*—These are so called, as being analogous to the effects of ordinary electricity. An active broken circuit produces the phenomena of electric repulsion, as already stated (page 149). A Leyden phial may also be charged by contact of its inner coating with one wire of the circle, while the outer communicates either with the other wire or with the ground: a full charge, though of feeble intensity, is almost instantly given. On approximating the wires of an active circle, a brilliant spark passes between them just before contact, as well as in the act of breaking contact. When the electric current is made to pass through the body of an animal, as on holding the conducting wires in the hands, previously moistened to facilitate conduction, a dis-

tinct shock is felt, which is powerful when a battery of high tension is employed. On sending the current through fine metallic wires or slender pieces of plumbago or compact charcoal, these conductors become intensely heated, the wires even of the most refractory metals are fused, and a vivid white light appears at the charcoal points equal, if not superior, in splendour to that of phosphorus burning in oxygen gas; a phenomenon in no wise referable to combustion, as it takes place in a vacuum or under water. If the electric current pass through thin metallic leaves, the metals burn with vivid scintillations:—gold leaf emits a white light tinged with blue, silver a beautiful emerald green light, copper a blueish white light with red sparks, lead a rich purple, and zinc a brilliant white light fringed with red. In burning leaves, fusing wire, and igniting charcoal, a large quantity of electricity is the only requisite: the large battery of Children, though capable of fusing several feet of platinum wire, had an electric tension so feeble, that it did not affect the gold leaves of the electrometer, gave a shock scarcely perceptible even when the hands were moist, communicated no sensible charge to a Leyden jar, and could not produce chemical decomposition. If the quantity and intensity of the current are both great, an arc of light appears between the charcoal points after contact, even through an interval of an inch or more.

The electrical effects of galvanism are so similar to those of the electrical machine, that it is impossible to witness and compare both series of phenomena without referring them to the same agent. The question of identity early occupied the attention of Wollaston, who made some very beautiful and conclusive experiments to prove that not only are the electrical effects of the machine producible by galvanism, but that the chemical effects of galvanism may be characteristically produced by a current from the electrical machine (Phil. Trans, 1801). The subject has been examined anew by Faraday, who has subjected the effects of electricity and galvanism to a minute and critical comparison: he has obtained ample proof of the decomposing power of an electric current from an electrical machine, both by repeating the experiments of Wollaston and devising new ones of his own. He has also completed the chain of evidence by deflecting a magnetic needle with an electric current from the machine; an observation, indeed, which had been previously made by Colladon. These researches

have led to a remarkable contrast between the quantity of electricity concerned in the production of voltaic and ordinary electrical phenomena. Faraday states that the quantity of electric fluid employed in decomposing a single grain of water is equal to that of a very powerful flash of lightning; and this statement, surprising as it is, is supported by such strong evidence, that it is difficult to withhold assent to the assertion.

II. *Magnetic Effects of Galvanism.*—The power of lightning in destroying and reversing the poles of a magnet, and in communicating magnetic properties to pieces of iron which did not previously possess them, was noticed at an early period of the science of electricity, and led to the supposition that similar effects may be produced by the common electrical and voltaic apparatus. Attempts were accordingly made to communicate the magnetic virtue by means of electricity and galvanism; but no results of importance were obtained till the winter of 1819, when Oersted of Copenhagen made his famous discovery, which forms the basis of a new branch of science. (An. Phil. xvi. 273.)

The fact observed by Oersted was, that the metallic wire of a closed voltaic circle,—and the same is true of charcoal, saline fluids, and any conducting medium which forms part of a closed circle,—causes a magnetic needle placed near it to deviate from its natural position, and assume a new one, the direction of which depends upon the relative position of the needle and the wire. On placing the wire above the magnet and parallel to it, the pole next the negative end of the battery always moves westward; and when the wire is placed under the needle, the same pole goes towards the east. If the wire is on the same horizontal plane with the needle, no declination whatever takes place; but the magnet shows a disposition to move in a vertical direction, the pole next the negative side of the battery being depressed when the wire is to the west of it, and elevated when it is placed on the east side. Ampère has suggested a useful aid for recollecting the direction of these movements. Let the observer regard himself as the conductor, and suppose a positive electric current to pass from his head towards his feet, in a direction parallel to a magnet; then its north pole in front of him will move to his right side, and its south pole to his left. The plane in which the magnet moves is always parallel to the plane in which the observer supposes himself to be placed. If the plane of his chest is horizontal, the plane

of the magnet's motion will be horizontal; but if he lie on either side of the horizontally suspended magnet, his face being towards it, the plane of his chest will be vertical, and the magnet will tend to move in a vertical plane.

The extent of the declination occasioned by a voltaic circle depends upon its power, and the distance of the connecting wire from the needle. If the apparatus be powerful, and the distance small, the declination will amount to an angle of 45° . But this deviation does not give an exact idea of the real effect which may be produced by galvanism; for the motion of the magnetic needle is counteracted by the magnetism of the earth. When the influence of this power is destroyed by means of another magnet, the needle will place itself directly across the connecting wire; so that the real tendency of a magnet is to stand at right angles to an electric current.

The communicating wire is also capable of attracting and repelling the poles of a magnet. This is easily demonstrated by permitting a horizontally suspended magnet to assume the direction of north and south, and placing near it the conducting wire of a closed circle, held vertically and at right angles to the needle, the $+$ current being supposed to flow from below upwards. When the wire is exactly intermediate between the magnetic poles, no effect is observed; on moving the wire nearly midway towards the north pole, that is, to the pole which points to the north, the needle will be attracted; and repulsion will ensue when the wire is moved close to the north pole itself. Similar effects occur on advancing the wire towards the south pole. Such are the phenomena if the $+$ current ascend on the west side of the needle; but they are reversed when the wire is placed vertically on the east side. Attractions and repulsions likewise take place in a dipping needle, when the current flows horizontally across it.

The discovery of Oersted was no sooner announced, than the experiments were repeated and varied by philosophers in all parts of Europe, and, as was to be expected, new facts were speedily brought to light. Among the most successful of those who early distinguished themselves were Ampère, Biot, and Arago, of Paris, and Davy and Faraday in this country. A host of other able men have since added their contributions; and their joint labours have established an altogether new science, *Electro-Dynamics*, which has already become one of the most important branches of physical

knowledge, and still offers a rich harvest of discovery to its cultivators. Those who wish to enter deeply into the study of this subject should consult the *Recueil d'Observations Electro-Dynamiques* by Ampère, Cumming's Manual of Electro-Dynamics, Murphy's Treatise on Electricity, and the second edition of Barlow's Essay on Magnetic Attractions. A less mathematical, and therefore more generally intelligible, treatise has been drawn up with great ability by Roget, and published as part of the Library of Useful Knowledge; and a Popular Sketch of Electro-Magnetism has been given by Watkins of Charing-cross. To these works I refer as supplying that detail of the facts and theories of electro-dynamics, which, as belonging more to the province of physics than chemistry, is unsuited to the design of this volume. My object is merely to give an outline of the discoveries in electro-dynamics, and to convey an idea of the nature and present state of the Science.

The phenomena of electro-dynamics are solely produced by electricity in motion. Accumulated electricity giving rise to tension, which acts so essential a part in experiments with the electrical machine, has no influence whatever on a magnetic needle. The passage of electricity through solid or liquid conductors is essential; and it is remarkable that the more freely the current is transmitted, that is, the more perfect the conducting substance, the more energetic is its deflecting power. In fact, a magnetic needle is a *galvanoscope*, by which means the existence and direction of an electric current may be detected. It was early employed with this intention by Ampère, who found that a voltaic apparatus itself acts on a magnetic needle placed upon or near it in the same manner as the wire which unites its two extremities; but as the deflection took place only when the opposite ends of the battery were in communication, and ceased entirely when the circuit was broken, he inferred that electricity passes uninterruptedly through the battery itself when the circuit is closed, and not at all in the interrupted circuit.

But a magnetic needle will not only indicate the existence and direction of an electric current: it may even serve, by the degree of deflection, as an exact measure of its force. When used for this purpose, under the name of *galvanometer*, some peculiar arrangements are required in order to ensure the requisite delicacy and precision. Experiment proves that a magnet is equally affected by every point of a conductor along which an electric current is

passing; so that a wire transmitting the same current will act with more or less energy, according as the number of its parts contiguous to the needle is made to vary. On this principle is constructed the *Galvanometer* or *Multiplier* of Schweigger. A copper wire is bent into a rectangular form consisting of several coils, and in the centre of the rectangle is placed a delicately suspended needle, as shown in figure 17. Each coil adds its influence to that of the others; and as the current, in its progress along the wire, passes repeatedly above and below the needle in opposite directions, their joint action is the same. In order to prevent the electricity from passing laterally from one coil to another in contact with it, the wire should be covered with silk. The ends

Fig. 17.

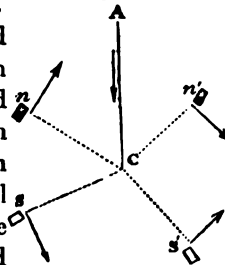


of the wire, *a* and *b*, are left free for the purpose of communication with the opposite ends of the voltaic circle. When a single needle is employed, as shown in the figure, its movements are influenced partly by the earth's magnetism, and partly by the electric current. The indications are much more delicate when the needle is rendered *astatic*, that is, when its directive property is destroyed by the proximity of another needle of equal magnetic intensity, fixed parallel to it, and in a reversed position, each needle having its north pole adjacent to the south pole of the other: in this state the needles, neutralizing each other, are unaffected by the magnetism of the earth, while they are still subject to the influence of galvanism. If, as in the last figure, the lower needle lie within the rectangle, and the upper needle just above it, the electric current flowing between will act on both in the same manner. For researches of delicacy the needle should be suspended by a slender long thread of glass, and the deflecting force measured, not by the length of the arc traversed by the needle, but by the torsion required to keep the needle at a constant distance from the wire, as in the torsion electrometer of Coulomb (page 128). A very valuable instrument on this principle has been described by Ritchie (Royal Inst. Journal, N. S. i. 81).

The mutual influence of a magnetic pole and a conducting wire changes with the distance between them. Experiment shows that the action of a magnetic pole and a continuous conductor, every point of which exerts a separate energy on the pole, varies inversely as the distance. This result justifies the opinion that the force of a magnetic pole on a *single* point of a conductor varies as the square of the distance, the same law which regulates the distribution of heat and light, as well as the effects due to electricity.

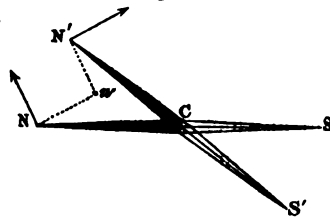
From some of the experiments of Oersted above mentioned, it was at first believed that a force, one while attractive and at another repulsive, acted in straight lines between the magnet and conducting wire; but on examination all the phenomena are found referable to a force acting tangentially upon the poles of a magnet, and in a plane perpendicular to the direction of the current. Place, for instance, a blank card flat on the table, and fix a wire A C upright in its centre. If, then, a positive electric current pass up or down the wire, a magnetic pole resting on the card will be inclined to move in the plane of the card, and therefore at right angles to the current, and to describe a circle round C as its centre. If a north pole be at n and n' , and a south pole at s and s' , and a + current descend as shown by the arrow in figure 18, let fall from each pole a dotted line perpendicular to the wire at C, and each dotted line will be the radius of the circle in which the corresponding pole will rotate. All the north poles will move in the line of the tangent directed to the right of the radius, and will have the same course as the hands of a watch when it is placed on a table with the dial plate upwards; and the south poles will rotate in the opposite direction. Should the electric current be ascending, the rotation of each pole will be reversed. If the current move horizontally, the plane of rotation will be vertical; and if figure 18 be moved into this position, the positive current still flowing from A to C, the arrows on the card will still indicate the course of rotation.

Fig. 18.



The movements first observed by Oersted (page 155) are referable to this principle. When a magnetic needle, movable round the middle of its axis, is acted on by a parallel current, its poles receive an equal but contrary impulse, and the needle consequently comes to rest across the direction of the current. If a vertical + current be placed, as shown in figure 19, at w , on the right side of a horizontal needle N S, movable round C, the pole N will move towards it; but if the current con-

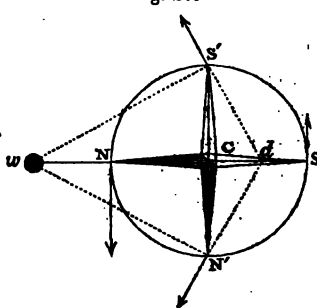
Fig. 19.



tinue at w while the magnet occupies the position of $N' S'$, the pole N will recede from the current: thus there is the appearance of repulsion in one case and of attraction in the other.

If a similar current were without the circle in which a horizontal magnet moves, as at w in figure 20, then the magnet, stationary at $N S$, would at first have its poles impelled in opposite directions; but when it reaches the position $N' S'$, the force at each pole acts on the same side of the magnet's axis. The poles also, being equidistant from w , and having the same inclination, will be influenced by equal forces acting at the same mechanical advantage. They

Fig. 20.



will therefore, by the laws of equilibrium, have a resultant which will pass directly through the centre of motion. This resultant, represented as applied at d , will tend to draw the wire w and the middle of the magnet C directly towards each other.

Fig. 21.

If the conducting wire w were on the right instead of the left side of the magnet, as in figure 21, then the resultant, passing as before through the centre of motion, but in an opposite direction, tends to draw the magnet and wire directly from each other, and to give the appearance of repulsion.

The same principle accounts for the rotation of a magnetic pole round a current, discovered by Faraday. Into the centre of the bottom of a cup, as in the vertical section, figure 22, a copper wire $c d$ was inserted, a cylindrical magnet $n s$ was attached by a thread to the copper wire c , and the cup was nearly filled with mercury, so that pole n only of the magnet projected. A conductor $a b$ was then fixed in the mercury perpendicularly over the wire c . On connecting the conducting wires with the opposite ends of a battery, a current was transmitted from one wire through the mercury to the other. If the + current descend, the north pole of the

Fig. 22.



magnet, if uppermost, will rotate round the wire $a b$, passing from east through the south to west like the movements in the hands of a watch; and if the current ascend, the line of rotation will be reversed. Under similar circumstances the south pole would in each case rotate in the opposite direction.

If a magnetic pole rotate round a conductor, a conductor will be equally disposed to rotate round a magnetic pole, just as a magnet moves towards iron or iron towards a magnet, according as one or other is free to move. Accordingly, on fixing a magnet vertically in the middle of a cup of mercury, fig. 23, and transmitting a current by the movable conductor $a b$ through the mercury, and along a second conductor d , fixed as before in the bottom of the cup, Faraday found that the free extremity b of the wire moved round the pole of the magnet in a direction similar to the last.

Fig. 23.



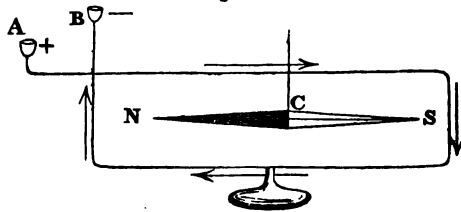
It is obvious that the direction of rotation imparted by a fixed current to the movable pole, will be identical with that which the same pole tends to impart to the same current. Thus let w in figure 24 represent the section of a wire along which a + current is descending, and n the north pole of a magnet. If w impel n towards the right side, n will give an impulse to w in the opposite direction, as indicated by the arrows. Each is disposed to describe a circle round the other as a centre, moving in the same direction as the hands of a watch with its dial upwards; and if w and n were equally free to move, they would act as a couple in statics, and tend to rotate round the middle of the dotted line which joins them.

Fig. 24.



The advantage of the rectangular form in the construction of a galvanometer (page 158) will now be intelligible. A magnetic needle NS , pointing north and south, and suspended by the point C horizontally within the rectangle, figure 25, will

Fig. 25.

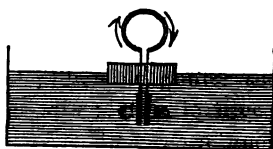


M

be influenced in the same manner by each of its sides. If the + current flow from A horizontally above the needle from north to south, and then successively along the other three sides up to B, the separate influence of each side, agreeably to the principle above illustrated, will impel the north pole eastward, and the south to the west. The little cups A B are designed to contain mercury, and afford a ready means of connecting the rectangle with the opposite sides of a galvanic combination.

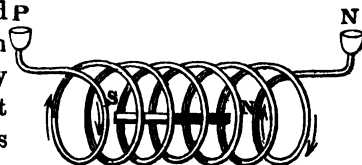
If the rectangle, in the last combination, have the property of impelling the north pole of a magnet to its right side, the north pole, when placed on that side, will give an opposite impulse to the rectangle. This may be shown by an elegant apparatus of De la Rive, which consists of a circular copper wire, the extremities of which are passed through a cork, and soldered to a plate of zinc and copper. On placing the arrangement in a vessel of acidulated water, a positive electric current passes from the copper plate round the circle to the zinc, as shown in figure 26; and as the cork renders the apparatus buoyant, a very slight force will throw it into motion. It will exhibit various phenomena of attraction and repulsion, all explicable on the principle already explained, according to the relative position of the magnetic pole which is presented. The apparatus will be more powerful if the conducting wire, covered with silk to prevent lateral communication, be formed into several circles of the same diameter, on the principle of the multiplier.

Fig. 26.



A current of voltaic electricity not only determines the position of a magnet, but renders steel permanently magnetic. This was observed nearly at the same time by Arago and Davy, who found that when needles are placed at right angles to the conducting wire, permanent magnetism is communicated; and Davy also succeeded in producing this effect even with a shock of electricity from a Leyden phial. Arago, at the suggestion of Ampère, made a voltaic conductor into the form of a helix, into the axis of which he placed P a needle, as in figure 27. As in this arrangement the current nearly in every part of its course is at right angles to the needle, and as

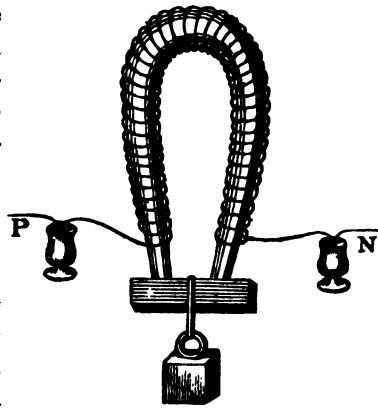
Fig. 27.



each coil adds its effect to that of the others, the united action of the helix is extremely powerful. The needle was thus fully magnetized in an instant.

Though soft iron does not retain magnetism, its magnetic properties while under the influence of an electric current are very surprising. A piece of soft iron about a foot long and an inch in diameter is bent into the form of a horse-shoe, a copper wire is twisted round the bar at right angles to its axis, and an armature of soft iron, to which a weight may be attached, is fitted to its extremities, as in figure 28. On

Fig. 28.

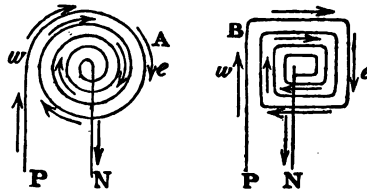


connecting the ends of the wire with a simple voltaic circle, even of small size, the soft iron instantly becomes a powerful magnet, and will support considerable weights. Increasing the number of coils gives a great increase of power; but as the length of wire required for that purpose diminishes the influence of the current (page 152), the following arrangement has been successfully adopted. The total length of copper wire intended to be used is cut into several portions, each of which, covered with silk or cotton thread to prevent lateral communication, is coiled separately on the iron. The ends of all the wires are then collected into two separate parcels, and are made to communicate with the same voltaic battery, taking care that the + current shall pass along each wire in the same direction. The current is thus divided into a number of branches, and has only a short passage from one end of the battery to the other, though it gives energy to a multitude of coils. A combination of this kind, connected with a battery of five feet square, supported 2063 pounds, or nearly a ton weight.

In witnessing the influence of voltaic conductors over the directive property of magnets, and in inducing magnetism, it is difficult to divest one's self of the conviction that these conductors, while transmitting a current, are themselves magnetic. This belief was early entertained by those who repeated the experiments of Oersted, and experimental evidence of its truth was speedily adduced.

Arago and Davy found that a copper wire connecting the end of a voltaic combination attracted iron filings, but that they instantly fell off as soon as the circuit was broken ; and a conductor, when its movements were not impeded by friction or gravity, was proved by Ampère to be obedient, like an ordinary magnet, to the magnetic agency of the earth. Though these properties may be exhibited by a single wire, the action is more conspicuous when, on the principle of the multiplier, the conductor is twisted into a spiral,

Fig. 29.

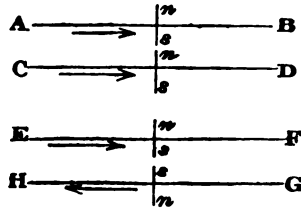


as A, figure 29, or into a rectangular form as represented by B in the same figure. When the arrangement is connected with a floating galvanic combination, as in figure 25, or is very delicately suspended, the plane of the spiral places itself east and west, the + current ascending on the west side and descending on the east : the + current, in fact, takes the same course as the hands of a watch when it is held on edge with the plane of the dial lying east and west, facing the south. That side of the spiral which is towards the north, consistently with an experiment already mentioned (page 161), acts as the north pole ; and the south side of the spiral has an opposite polarity. Each side is powerfully attractive to iron filings. Another convenient form of the conductor is the helix, figure 27. Each coil of the helix is a separate magnet, and tends to place itself in the same position as the spiral or rectangle ; but the multiplied effect of all the coils causes north and south polarity to be accumulated at the opposite ends of the helix, and therefore to be separated, not by the mere thickness of the wire, but by the whole length of the helix.

Since, therefore, the conductors just described may be regarded as magnets, such magnetized conductors ought mutually to repel or attract each other, when poles of the same or a different nature are adjacent ; and as the action of a whole spiral or rectangle is merely the accumulated effect of its individual parts, it is fair to presume that each small portion of a conductor has its opposite sides in a state of opposite polarity, and that two such contiguous portions should attract or repel each other on the same principle as the spirals of which they constitute a part. Nay, even different parts of the same conductor ought to be mutually attractive or repulsive.

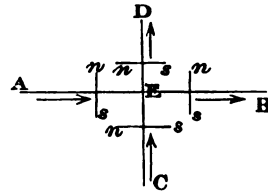
These inferences from the facts already detailed were fully demonstrated by Ampère soon after the discovery of Oersted. He proved that two voltaic conductors, or two portions of the same conductor, attract each other when the currents have the same direction, and are mutually repulsive when they are traversed by opposite currents; which is exactly what would be anticipated from the magnetic influence of conductors. Thus, in the two parallel positive currents, AB and CD, figure 30, which flow in the same direction, the contiguous sides are affected with an opposite polarity, one being south and the other north; whereas in the two contrary currents, EF and GH, the adjacent sides have the same polarity, and therefore repel each other.

Fig. 30.



Similarly when two currents cross each other, as AB and CD, figure 31, it is obvious that at two of the four corners, AD and CB, similar poles are contiguous; while at the other corners different poles concur. Hence the wires tend to revolve round E, and place themselves parallel to the currents, so that both may flow in the same direction.

Fig. 31.



If a moveable conductor CD be wholly on one side of AB, as in figure 32, repulsion will ensue on one side, and attraction on the other. The direction in which these forces act is indicated by the dotted arrows, eb and eg ; and they give a resultant, er , which tends to draw CD to the right side.

Fig. 32.

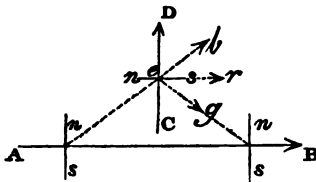


Fig. 33.

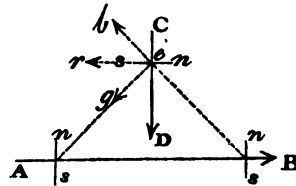
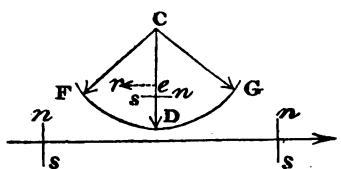


Figure 33 shows the effect of reversing the current in CD, which will consequently be drawn by a force at right angles to itself to the left side.

If in the last case the conductor CD were moveable round C as a centre, then the resultant er would draw D towards F, figure 34; but if the current in either conductor were reversed, CD would tend to rotate towards G.

Fig. 34.



These are a few examples of the numerous facts experimentally proved by Ampère concerning the action of voltaic conductors on each other. It is to this branch of the subject the term of *Electro-Dynamics*, or the science of electricity in motion, is sometimes restricted, while the mutual action of conductors and magnets is called *Electro-Magnetism*; but these two branches are so entirely parts of the same science, that I have included both under Ampère's term of *Electro-Dynamics*. Any one who has studied the few preceding pages with moderate care, cannot fail to trace a close analogy between a helix traversed by an electric current and a magnet. The former is affected by other voltaic conductors, by the poles of a magnet, and by the magnetism of the earth, in the same manner as the latter. It was this similarity, or rather identity, of action which led Ampère to his theory of magnetism. He supposes that the polarity of every magnet is solely owing to the circulation, within its substance and at its surface, of electric currents, which continually pass around all its particles in planes perpendicular to its axis. On placing a magnet in its natural position of north and south, the direction of its currents is exactly the same as in the conductors of figure 29, descending on the east side, passing under the magnet from east to west, and ascending on the side next the west. In like manner are currents supposed to circulate within the earth, especially near its surface, passing from east to west in planes parallel to the magnetic equator. These terrestrial currents cause all bodies, which are freely suspended, and are possessed of electric currents, to place themselves in such a position that the current on their under side should flow in parallelism, and in the same direction, with that in the earth immediately beneath. That the existence of such currents will account for the directive property of the earth, follows from the mutual action of conductors; and Barlow, to render the analogy still more complete, constructed a hollow sphere of wood in which electric currents were made to circulate in the same direction as they are thought to do in the earth;

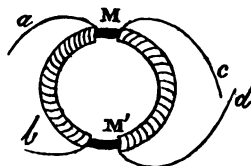
and by placing an astatic needle on different parts of its surface, he found that all the phenomena of terrestrial magnetism might be imitated. Observation has even supplied a cause for the existence of currents in the earth, moving in the direction which theory requires. The diurnal rotation of our planet on its axis exposes its surface to be heated in a direction passing from east to west; and the discoveries which have been made in thermo-electricity (page 118) sufficiently prove the probability of electric currents being established in the conducting matter of the earth by the successive heating of its parts. In short, the theory of Ampère connects the facts of electro-dynamics with the phenomena of terrestrial magnetism, and affords a splendid instance of the application of mathematical analysis to physical research.

Volta-electric Induction.—The developement of electricity by the vicinity of an excited body, already described under the name of induced electricity (page 122), led Faraday to inquire whether electricity in motion, as well as that of tension and at rest, may not be excited by induction. Though baffled in his early attempts, he at last succeeded in laying open a new branch of electro-dynamics, which vies in interest and importance with the fundamental discovery of Oersted (Phil. Trans. 1831). A copper wire 203 feet long was passed in form of a helix round a large block of wood, and an equal length of a similar wire was wound on the same block and in the same direction, so that the coils of each helix should be interposed, but without contact, between the coils of the other. The ends of one of the helices were connected with a galvanometer, and the other with a strong galvanic battery, with the view of ascertaining whether the passage of an electric current through one helix would induce a current in the adjoining helix. It was found that the galvanometer needle indicated a current at the moment both of completing and breaking the circuit, but that in the interval no deflection took place; and similarly the induced currents readily magnetized a sewing needle, while the electric current along the inducing helix was in the act of beginning or ceasing to flow, but at no other period. By varying the experiment, the same result was obtained: an electric current transmitted from a voltaic battery through a conducting helix does not induce a current in an adjoining helix, except at the moment of making or breaking the voltaic circuit. In the former case the direction of the induced current is opposite to that of the inducing current, and in the latter

case it is the same. This phenomenon is distinguished by Faraday under the name of *volta-electric induction*.

The inducing power of a magnet greatly exceeds that of an electric current. A ring of soft iron was covered to nearly half its extent by several helices, the ends of which were brought together so as to constitute a compound helix terminating in the conductors *a b*, figure 35; and on the other half of the ring were arranged similar helices which communicated by *c d* with a galvanometer. The two sets of helices were thus separated from each other by portions of the ring *M M'*, and were protected by cloth from direct contact with the ring itself. At the moment the wires *a b* touched the ends of a voltaic combination, the galvanometer was strongly affected: the needle then returned to its former position and remained there until the voltaic circuit was broken, when the needle was again deflected as strongly as before, but in the opposite direction. The action was still greater when both compound helices were on the same part of the ring, the induction being increased apparently by the closer contiguity of the helices. Another of Faraday's arrangements, which was in several respects more convenient than the ring, consisted of a hollow cylinder of pasteboard, round which two compound helices were adjusted. On connecting one helix with a voltaic combination, the other deflected the galvanometer and magnetized a needle, as in the experiments of volta-electric induction at first described; but when a cylinder of soft iron was introduced into the pasteboard case, and a voltaic current transmitted as before, the effect on the galvanometer was much greater. The action in this last experiment and with the iron ring is distinguished by the name of *Magneto-electric induction*.

Fig. 35.



The phenomena arising from magneto-electric and volta-electric induction are manifestly owing to the same condition of the induced wire: the action on the needle, though different in force, is identical in kind. It is equally clear that the agent brought into operation in the induced wire is an electric current, or, to dismiss the language of theory, that the induced wire is in the same electric state as the conducting wire in a closed voltaic circle. Its power in magnetizing steel and deflecting a magnet is sufficient evidence of this; but Faraday, by magneto-electric induction, succeeded in

throwing a frog's leg into spasms by connecting it with the induced wire, and by arming the ends of that wire with points of charcoal, and separating them at the instant the galvanic circuit of the inducing wire was broken or restored, sparks of electricity were obtained. The mode in which soft iron contributes to the effect is likewise obvious. An electric current circulating round a bar of soft iron has been shown to convert it into a temporary magnet possessed of surprising power (page 162); and it is doubtless to this magnet, called into temporary existence by the electric current, most of the induced electricity is to be ascribed. Faraday reduced this to certainty by surrounding a cylinder of soft iron with one helix connected with the galvanometer, and converting the soft iron into a temporary magnet, not by a voltaic battery, but by placing at each end of the cylinder the opposite pole of a magnet. During the act of applying the magnetic poles to the iron, the galvanometer needle was deflected; and the deflection was reproduced, but in the opposite direction, when the magnetism of the iron was ceasing by the removal of the magnet. Similarly, when a helix was wound on a hollow cylinder of pasteboard, and a real magnet was introduced, the galvanometer was deflected: the needle then remained quiescent so long as the magnet was left in the cylinder; but in the act of its removal, the needle was again deflected, though, as usual, in the opposite direction.

These singular phenomena, which establish such new and intimate relations between voltaic and magnetic action, and supply additional evidence in favour of Ampère's beautiful theory of magnetism, have led to an experiment by which, at first view, an electric spark appeared to be derived from the magnet itself. After Faraday had announced his experiment, above mentioned, of obtaining a spark from the induced wire, other attempts were made to effect the same object with a magnet, without the aid of galvanism. The first person who succeeded in this country was Forbes, who operated with a powerful loadstone (Phil. Trans. Ed. 1832). A helix of copper wire was formed round the middle of a cylinder of soft iron, which was of such length that its extremities reached from one pole of the loadstone to the other. On applying and withdrawing the soft iron cylinder to and from the poles of the loadstone, magnetism was alternately created and destroyed within it. At these periods of transition, electric currents were induced in the helix surrounding the soft iron; and when, at these instants, me-

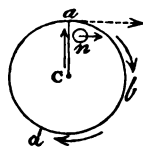
tallic contact between the conducting wires of the helix was broken, an electric spark was visible. Forbes succeeded best by connecting one wire with a cup of mercury, and removing the other wire from contact with its surface at the instant when an assistant withdrew the armature of soft iron from the loadstone. In this experiment, therefore, the electricity was obtained from the helix, and was induced in it by the soft iron while in the act of acquiring or losing magnetism. The same experiment was performed by Faraday with a loadstone belonging to Daniell; and shortly before the experiment of Forbes, Nobili and Antinori succeeded with an ordinary steel magnet. Pixii in Paris afterwards performed this experiment with great effect by causing a strong horse-shoe magnet to revolve upon an axis, its poles passing in rapid succession in front of a soft iron armature of the same form; and a still better arrangement is to cause the armature to revolve in front of the poles of a powerful magnet, as in the instrument fitted up by Saxton, and exhibited at the Adelaide-rooms, London. The voltaic currents are induced in one direction as the armature approaches the magnetic poles, and are reversed as it quits them; so that the currents change their direction twice in each revolution. On all these occasions the source of the electricity is the same, being always induced in the helix by a temporary magnet; and it has all the characters of a voltaic current. It produces brilliant sparks, renders platinum wire red hot, and gives a strong shock. It readily explodes gunpowder; and Ritchie has fitted up an apparatus for exploding with it a mixture of oxygen and hydrogen gases. It decomposes water rapidly; and though from the rapid reversal in the direction of the currents, both gases are given off at the same wire, Pixii succeeded in collecting them separately. (*An. de Ch. et Ph.*)

Intimately associated with magneto-electric induction, if not referable to the very same origin, is the induction of electric currents by movement. On introducing a magnet into a hollow helix of copper wire, as also on withdrawing the magnet after its introduction, an electric current was momentarily induced in the wire; and if, the magnet being stationary, the helix were moved in its vicinity, an electric current is likewise induced. The action is not confined to magnets and copper wire; but in all solid conductors of electricity, when moved near the pole of a magnet, an electric current is generated, and the most perfect conductors act with the greatest effect. The direction of the movement is not immaterial: it is

essential that the plane in which the conductor moves should form an angle with the axis of the magnet; and the most powerful currents were induced, when the plane of motion was at right angles to that axis, and hence parallel to the electric currents which Ampère supposes to exist in the magnet. The direction of the currents depends on the direction of motion. If the movement of a wire from right to left cause a certain current, an opposite current will be induced when the wire is moved from left to right. In short, with regard to the direction of an induced current, Faraday's researches establish this law, deduced by Ritchie: if a wire conducting voltaic electricity produce on magnets or conductors certain motions, whether repulsive, attractive or rotatory, and if the battery be removed, the ends of the wires brought into metallic contact, and the same motions be produced by mechanical means, the conductor will have the same electric state induced in it as it had when connected with the battery. (Phil. Mag. 3rd series, iv. 12.)

Faraday has applied this principle in a most happy manner to explain the phenomena of rotation discovered by Arago. If a plate of copper be revolved close to a magnetic needle suspended so that it may rotate in a plane parallel to the plate, the needle will rotate in the same direction; and, reciprocally, a rotating magnet tends to give rotation to a contiguous copper plate. The same effects are produced by the rotation not only of all metals, but, according to Arago, of all bodies whether solid, liquid, or gaseous. These effects, which Faraday has principally examined in reference to the rotation of metals, are entirely owing to electric currents induced by the rotation, and flowing at right angles to the direction of motion. Suppose $a b d$, figure 36, to be a circular metallic plate, placed horizontally, and capable of revolving round its centre c ; and let n be the north pole of a magnet situated above the plate near its circumference at a . If a positive electric current were to flow along the plate from c to a , the pole n would be impelled at right angles in the direction indicated by the arrow; and hence, if the plate were made to revolve in the same direction, indicated by the arrows at b and d , an induced positive current would instantly flow from c to a . Its direction would be constantly in that line, being at right angles to the dotted arrow, which indicates the direction in which that part of the plate nearest to the pole is moving. Hence

Fig. 36.



the pole, acted on by the induced current, would receive an impulse in the same direction.

If motion in the vicinity of a magnet induce an electric current, the same effect would be anticipated from the magnetic influence of the earth; and this fact has been proved by Faraday by most decisive and interesting experiments. When a bar of soft iron is held in the position of the dipping needle, the direction of which, in regard to terrestrial magnetism, is analogous to the axis of a common magnet, it acquires magnetic properties; and accordingly, on introducing a soft iron cylinder into a hollow helix of copper placed in the line of the dip, a galvanometer connected with the helix was instantly affected. But the use of iron may be dispensed with altogether; for when a helix of copper wire was simply moved at right angles to the dipping needle, electric currents were induced by the magnetism of the earth. The form of a helix is not even necessary: the movement of a piece of copper wire across the line of dip developed currents in the wire. The same effect was produced by the rotation of a copper plate placed horizontally so as to be nearly at right angles to the line of dip; and the revolution of a copper globe acted in the same manner. Faraday concludes that the rotation of the earth on its axis ought similarly to influence the conducting matters of its surface; and that electric currents should be thereby induced from the equatorial regions to either pole. He throws out the suggestion whether the aurora borealis and australis may not be produced by the returning currents passing from the poles of the earth into the atmosphere.

III. *Chemical Effects of Galvanism.*—The chemical agency of the voltaic apparatus, to which chemists are indebted for a most powerful instrument of analysis, was discovered by Carlisle and Nicholson, soon after the invention was made known in this country. The substance first decomposed by it was water. When two gold or platinum wires are connected with the opposite ends of a battery, and their free extremities are plunged into the same cup of water, but without touching each other, hydrogen gas is disengaged at the — and oxygen at the + wire. By collecting the gases in separate tubes as they escape, they are found to be quite pure, and in the exact ratio of two measures of hydrogen to one of oxygen. When wires of a more oxidable metal are employed, the result is somewhat different. The hydrogen gas

appears as usual at the — wire ; but the oxygen, instead of escaping, combines with the metal, and converts it into an oxide.

This important discovery led many able experimenters to make similar trials. Other compound bodies, such as acids and salts, were exposed to the action of galvanism, and all of them were decomposed without exception, one of their elements appearing at one side of the battery, and the other at its opposite extremity. An exact uniformity in the circumstances attending the decomposition was also remarked. Thus, in decomposing water or other compounds, the same kind of body was always disengaged at the same side of the battery. The metals, inflammable substances in general, the alkalies, earths, and the oxides of the common metals, were found at the — wire ; while oxygen, chlorine, and the acids, went over to the + surface.

In performing some of these experiments, Davy observed, that if the conducting wires were plunged into separate vessels of water, made to communicate by some moist fibres of cotton or amianthus, the two gases were still disengaged in their usual order, the hydrogen in one vessel, and the oxygen in the other, just as if the wires had been immersed into the same portion of that liquid. This singular fact, and another of the like kind observed by Hisinger and Berzelius, induced him to operate in the same way with other compounds, and thus gave rise to his celebrated researches on the transfer of chemical substances from one vessel to another (Phil. Trans. 1807). In these experiments two agate cups, N and P, were employed, the first communicating with the —, the second with the + wire of the battery, and connected together by moistened amianthus. On putting a solution of sulphate of potassa or soda into N, and distilled water into P, the acid very soon passed over to the latter, while the liquid in the former, which was at first neutral, became distinctly alkaline. The process was reversed by placing the saline solution in P, and the distilled water in N, when the alkali went over to the — cup, leaving free acid in the other. That the acid in the first experiment, and the alkaline base in the second, actually passed along the amianthus, was obvious ; for on one occasion, when nitrate of oxide of silver was substituted for the sulphate of potassa, the amianthus leading to N was coated with a film of metal. A similar transfer was effected by putting distilled water into N and P, and a saline solution in a third cup placed between the two others,

and connected with each by moistened amianthus. In a short time the acid of the salt appeared in P, and the alkali in N. It was in pursuing these researches that Davy made his great discovery of the decomposition of the alkalies and earths, which till then had been regarded as elementary. (Phil. Trans. 1808.)

Such is a statement of the principal phenomena of electro-chemical decomposition according to the earlier experiments. The facts then observed were received as established truths of science, and passed current without suspicion or scrutiny till the present time. But Faraday, in his revision of this part of the science, has not only added much new matter, but proved that several points, which were considered as fundamental maxims, are erroneous. Before describing his results, however, I will define the new terms which he has had occasion to introduce.—In order to decompose a compound, it is necessary that it should be liquid, and that an electric current should pass through it; an object easily effected by dipping into the liquid the ends of the metallic wires which communicate with the voltaic circle. These extremities of the wires are commonly termed *poles*, from a notion of their exerting attractive and repulsive energies towards the elements of the decomposing liquid, just as the poles of a magnet act towards iron; and each is further distinguished by the term *positive* or *negative*, according as it affects an electrometer with + or — electricity. Now Faraday contends that these poles have not any attractive or repulsive energy, and act simply as a path or door to the current: he hence calls them *electrodes*, from *ηλεκτρον*, and *ὁδος*, a way. The electrodes are the surfaces, whether of air, water, metal, or any other substance, which serve to convey an electric current into and from the liquid to be decomposed. The surfaces of this liquid which are in immediate contact with the electrodes, and where the elements make their appearance, are termed *anode* and *cathode*, from *ἀνα*, upwards, and *ὁδος*, the way in which the sun rises, and *κατα*, downwards, the way in which the sun sets. The anode is where the + current is supposed to enter, and the cathode where it quits, the decomposing liquid, its direction, when the electrodes are placed east and west, corresponding with that of the + current which is thought to circulate on the surface of the earth (page 166). To *electrolyze* a compound, is to decompose it by the direct action of galvanism, its name being formed from *ηλεκτρον* and *λυω*, to *unloose or set free*; and an electrolyte is a compound which may

be electrolyzed. The elements of an electrolyte are called ions, from, *ion*, going, neuter participle of the verb to go. *Anions* are the ions which appear at the anode, and are usually termed the electro-negative ingredients of a compound, such as oxygen, chlorine, and acids; and the electro-positive substances, hydrogen, metals, alkalies, which appear at the cathode, are *cations*. Whatever may be thought of the necessity for some of these terms, the words electrode, electrolyze, and electrolyte, are peculiarly appropriate, and are already in use.

The principal facts determined by Faraday may be arranged under the following propositions:—

1. All compounds, contrary to what has been hitherto supposed, are not electrolytes, that is, are not directly decomposable by an electric current. But in making this assertion it is necessary to distinguish between primary and secondary decomposition. Water is an electrolyte, its hydrogen being delivered up at the — and its oxygen at the + electrode. A solution of hydrochloric acid is likewise an electrolyte, being resolved into chlorine and hydrogen. But nitric and sulphuric acids and ammonia are not electrolytes, though the first and last are decomposed by secondary action. Thus, on subjecting nitric acid to voltaic action, the water of the solution is electrolyzed, and its hydrogen arriving at the + electrode, decomposes the nitric acid, water being there reproduced and nitrous acid formed. So, in a solution of ammonia, the oxygen of decomposed water unites at the + electrode with the hydrogen of the ammonia, and nitrogen gas is evolved. Very numerous secondary actions are occasioned in this way, because the disunited elements are presented in a nascent form, which is peculiarly favourable to chemical action; and in many instances the electrode itself, which is commonly metallic, is chemically attacked. Thus, when chlorine is evolved against an electrode of gold, oxygen at one of some easily oxidable metal, as copper or iron, or sulphur against a silver electrode, chloride of gold, oxide of copper or iron, and sulphuret of silver, are generated. If these changes are caused by very feeble currents acting slowly, as for weeks, months, or years, the new products have opportunity to assume regularly crystalline forms. It is by such means that Becquerel has succeeded in procuring artificial minerals exactly resembling those which are found in mines (*Traité d'Electricité*); and Crosse has since obtained similar results (*Phil. Mag. and An.* ix. 229).

Taking these facts in conjunction with the researches of Fox on the electrical state of mineral veins, there can be no longer a doubt that feeble electric currents within fissures of rocks, induced by terrestrial magnetism, by variations of temperature at different parts of the rock, or by the different nature of the walls of the fissures, or of the solutions with which they are filled, may have been one principal source of metalliferous deposits; nor is it at all unreasonable or unphilosophical to suppose that the enormous mineral masses which now constitute our metalliferous veins may have been the work of such feeble currents acting during hundreds or thousands of centuries. Feeble agencies operative for a long period are often just as efficacious in effecting great changes as powerful agents at work during a short period; and Becquerel, in opening this new line of inquiry, has supplied a principle by which the scientific geologist may explain many of those obscure phenomena which fall within his observation.

2. Most of the salts which have been examined are resolvable into acid and oxide, apparently without reference to their proportions. But in compounds of two elements, the ratio of combination has an influence which has hitherto been wholly overlooked. No two elements appear capable of forming more than one electrolyte. Hydrochloric acid and fused metallic protochloride, such as the chlorides of lead and silver, and protochloride of tin, are readily decomposed; while bichloride of tin and other perchlorides resist decomposition. Substances which consist of a single equivalent of one element and two or more equivalents of some other element, are not electrolytes: this is the reason why sulphuric and nitric acid and ammonia do not yield primarily to voltaic action. This principle bids fair to become very important in determining which of several compounds of two elements contains single equivalents. Water, which is remarkable for its easy decomposition, may hence be inferred to be a true binary compound.

3. It has been ascertained that most of the elements are *ions*, and it is probable that all of them are so; but there are several important elements, such as nitrogen, carbon, phosphorus, boron, silicon, and aluminium, which have not yet been proved to be *ions*. This arises from the difficulty of obtaining these elements in compounds fitted for electrolytic action.

4. A single *ion*, that is, one ion not in combination with another, has no tendency to pass to either of the electrodes, and is

quite indifferent to the passing current, unless it be itself a compound ion, and therefore electrolyzable. The character of true electrolytic action consists in the separation of *ions*, one passing to one electrode and another to the opposite electrode, and appearing there at the same instant, unless the appearance of one or both be prevented by some secondary action.

5. There is no such thing as a transfer of *ions* in the sense usually understood. In order that the elements of decomposed water should appear at the opposite electrodes, there must be water between the electrodes; and for the similar separation of sulphuric acid and soda, there must be a line of particles of sulphate of soda extending from one electrode to the other. Thus, if a solution of sulphate of magnesia be covered with pure water, care being taken to avoid all admixture of particles, and the + metallic termination or pole touch the magnesian solution only, while the — pole is in contact with the water only, a deposit of magnesia occurs just where the pure water and the magnesian solution meet, and none reaches the — pole. In Davy's experiment, where sulphuric acid and soda appeared to quit each other, and pass over separately into a vessel of pure water, there was certainly by capillary attraction an actual transfer of the salt before decomposition occurred.

6. In the foregoing experiment a surface of water acts as the — electrode, clearly showing the contact of a metallic conductor with the decomposing liquid not to be essential. Faraday has proved that even air may serve as an electrode. A current from the prime conductor of an electrical machine was made to pass from a needle's point through air to a pointed piece of litmus paper moistened with sulphate of soda, and then to issue from a similarly moistened point of turmeric paper. True electrolytic action took place, the litmus becoming red and the turmeric paper brown, though both extremities of the decomposing solution communicated solely with a stratum of air.

7. Electro-chemical decomposition cannot occur unless an electric current is actually transmitted through the electrolyte; or, in other terms, an electrolyte is always a conductor of electricity. Water, which conducts an electric current, ceases to do so when it passes into ice, and then also resists decomposition—an observation equally true of all electrolytes on becoming solid. Moreover, liquids which resist electro-chemical decomposition do not permit

the current of a voltaic circle to pass. The alliance between conduction and decomposition is so constant, that the latter may be regarded as a means by which voltaic currents are transmitted through liquid compounds. Agreeably to this notion, solidity may interfere with conduction by chaining down the elements of a compound, and thereby preventing their transfer to the electrodes. Improving the conduction of a liquid, as by adding sulphuric acid to pure water, increases the decomposing power of a voltaic circle, the exciting fluid within the apparatus remaining the same; and Faraday has proved that the quantity of a compound decomposed is exactly proportional to the quantity of electricity which passes, however much other circumstances, such as the size of electrodes and conducting wires, number and size of plates, and nature of exciting fluid, may vary. Changes in these conditions do, indeed, influence the quantity of electricity transmitted; but then the degree of chemical decomposition varies in the same proportion. The foregoing facts at first led to the opinion that the current of a voltaic circle cannot pass through liquids, except those of a metallic nature, unless decomposition ensues at the same time; but Faraday has noticed that when the intensity is too feeble to effect decomposition, a small quantity of electricity may be transmitted, sufficient to be discovered by a galvanometer. This does not, however, essentially interfere with the law just announced.

8. Chemical compounds differ in the electrical force required for decomposition. A current of very feeble tension suffices to decompose iodide of potassium, while a much higher intensity is required for disuniting the elements of water. The order of easy decomposition in the annexed substances is as follows:—Solution of iodide of potassium; fused chloride of silver; fused protochloride of tin; fused chloride of lead; fused iodide of lead; solution of hydrochloric acid; and water acidulated with sulphuric acid. By extending tables of this kind, a ready method will be known for comparing the tension of voltaic circles.

9. The conduction of the electric currents within the cells of a voltaic circle depends on chemical decomposition equally with that between platinum electrodes. No substance not an electrolyte can serve to excite a voltaic apparatus; and for the passage of electricity from plate to plate through the intervening solution, the separation of substances previously combined in the required ratio is essential. Neither free oxygen nor a solution of chlorine can excite a current, though they attack the zinc and develop electricity;

and in a voltaic circle excited by dilute sulphuric acid, the electricity set in motion is due to decomposed water and oxidized zinc, and not at all to the union of the oxide of zinc with sulphuric acid. The platinum electrodes and intervening liquid may be viewed as one of the cells of the circle, except that the plates act merely as conductors, without any oxidation, the current passing in virtue of the decomposed solution. Thus, in figure 10, page 147, the zinc and copper plate of either of the glasses may be replaced by two plates of platinum; or several pairs of such plates may be introduced in any part of a compound circle, in which case the intervening spaces are cells of decomposition only. But such plates diminish very much the power of a battery. In the zinc and copper cells, the current is urged on by the appetency of the zinc and oxygen to unite; whereas, in passing between the electrodes, the electricity has to surmount the mutual attraction of oxygen and hydrogen, or some similar force, without the assistance of any opposing affinity. In overcoming this obstacle, the electric current is enfeebled; and if its tension be insufficient for decomposing the interposed liquid, it is almost completely arrested. Hence, in experiments on decomposition, the course of the electricity should be facilitated by employing large electrodes and wires, and placing them at a short distance from each other in a good conducting solution.

The principles above established show the importance of exciting all the cells of a voltaic circle with a liquid of the same strength. The electricity circulating in a voltaic apparatus with the conducting wires in contact, is equal to that which the feeblest cell is able to transmit, any chemical action in other cells more than sufficient for exciting that quantity being wasted; and in a circle with several decomposing cells, the current which traverses the cell of lowest conducting power determines the quantity circulating through the whole apparatus.

THEORIES OF GALVANISM AND ELECTRO-CHEMICAL THEORY.

Of the theories proposed to account for the developement of electricity in voltaic combinations, three in particular have attracted the notice of philosophers. The first originated with Volta, who conceived that electricity is set in motion, and the supply kept up, solely by contact or communication between the metals (page 138). He regarded the interposed solutions merely as conductors, by means of which the electricity developed by each pair of plates is conveyed from one part of the apparatus to the other.

Thus, in the pile or ordinary battery, represented by the following series.



Volta considered that contact between the metals occasions the zinc in each pair to be +, and the corresponding copper plate to be -; that the + zinc in each pair except the last, being separated by an intervening stratum of liquid from the - copper of the following pair, yields to it its excess of electricity; and that in this way each zinc plate communicates, not only the electricity developed by its own contact with copper, but also that which it had received from the pair of plates immediately before it. Thus, in the three pairs of plates contained in brackets, the second pair was thought to receive electricity from the first only, and the third pair from the first and second. In batteries constructed on the principle of the crown of cups (fig. 9), the *electro-motion*, as Volta called it, is ascribed to metallic communication between the zinc of one glass and the copper of the adjoining one.

The second is the *chemical theory*, proposed by Wollaston. Volta attached little importance to the chemical changes which never fail to occur in every voltaic circle, whether simple or compound, considering them as casual or unessential phenomena, and therefore neglected them in the construction of his theory. The constancy of their occurrence, however, soon attracted notice. In the earlier discussions on the cause of spasmodic movements in the frog (page 137), Fabroni contended, in opposition to Volta, that the effect was not owing to electricity at all, but to the stimulus of the metallic oxide formed or of the heat evolved during its production. More extended researches soon proved the fallacy of this doctrine; but Fabroni made a most ingenious use of the facts within his knowledge, and paved the way to the chemical theory of Wollaston.

Wollaston, fully admitting electricity as the voltaic agent, assigned chemical action as the cause by which it is excited. The repetition and extension of Volta's experiments by the English chemists speedily detected the error he had committed in overlooking the chemical phenomena which occur within the pile. It was observed that no sensible effects are produced by a combination of conductors which do not act chemically on each other; that the action of the pile is always accompanied by the oxidation of the zinc; and that the energy of the pile in general is proportional to the activity with which its plates are corroded. Observations of this

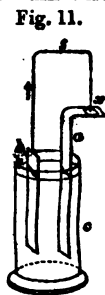
nature induced Wollaston to conclude that the process begins with the oxidation of the zinc,—that oxidation, or, in other terms, chemical action, was the primary cause of the development of electricity,—that the fluid of the circle served both to oxidize the zinc and to conduct the electricity which was excited,—and that contact between the plates served only to conduct electricity, and thereby complete the circuit.

The third theory of the pile was proposed by Davy, and is intermediate between the two former. He adduced many experiments in support of Volta's statement, that the electric equilibrium is disturbed by the contact of different substances, without any chemical action taking place between them. He acknowledged, however, with Wollaston, that the chemical changes contribute to the general result; and he maintained that, though not the primary movers of the electric current, they are essential to the continued and energetic action of every voltaic circle. The electric excitement was begun, he thought, by metallic contact, and maintained by chemical action.

The progress of inquiry since these theories first came into notice has gradually given more and more support to the views of Wollaston, and has at last, I apprehend, established it to the entire exclusion of the theory of Volta. The very fundamental position, that electricity is excitable as a primary result by the contact of different substances, is warmly contested, and, as some think with strong reason, has been disproved (page 120); but admitting, for the sake of argument, that a *small* effect, which is all that can now be contended for, may thus be produced, it is altogether insignificant when contrasted with the astonishing phenomena exhibited by a voltaic circle. The experiments of De la Rive, in reference to this question, appear irreconcilable with the theory of Volta (*An. de Ch. et Ph.* xxxviii. 225; lxi. 38; lxii. 147). This ingenious philosopher contends that the direction of a voltaic current is not determined by metallic contact, nor even by the nature of the metals relatively to each other, but by their chemical relation to the exciting liquid. As the result of his inquiries, he states, that of two metals composing a voltaic circle, that one which is most energetically oxidized will be + with respect to the other. Thus, when tin and copper are placed in acid solutions, the former, which is most rapidly corroded, gives a + current through the liquid to the copper, as the zinc does in the circle in fig. 1; but, if they are put into a solution of ammonia, which acts

most on the copper, the direction of the current will be reversed. Copper is + in relation to lead in strong nitric acid, which oxidizes the former most freely; whereas in dilute nitric acid, by which the lead is most rapidly dissolved, the lead is +. Even two plates of copper immersed in solutions of the same acid, but of different strength, will form a voltaic circle, the plate on which chemical action is most free causing a current of + electricity to the other: nay, it is possible to construct a compound circle solely with zinc plates and one acid solution (page 140), provided the same side of each plate be more rapidly oxidized than the other.

The admirable researches of Faraday (Phil. Trans. 1838 & 34) supply conclusive evidence against the theory of Volta, proving metallic contact not to be essential to voltaic action, inasmuch as it is procured characteristically without contact. A plate of zinc, *a*, fig. 11, about 8 inches long by $\frac{1}{2}$ an inch wide, was cleaned and bent at a right angle; and a plate of platinum, of the same width and 3 inches long, was soldered to a platinum wire *b s x*, the point of which, *x*, rested on a piece of bibulous paper lying upon the zinc, and moistened with a solution of iodide of potassium. On introducing the plates into a vessel, *c*, filled with dilute sulphuric and nitric acid, a + current instantly ensued in the direction of the arrow, as testified by the hydrogen evolved at the plate *a*, by the decomposed iodide of potassium, and by a galvanometer. We have thus a simple circle of the same construction and action as in figure 1, except in the absence of metallic contact.



Another proof, aptly cited by Faraday, of electric excitement being independent of contact, is afforded by the spark which appears, when the wires of a pair of plates in vigorous action are brought into contact. The spark is occasioned by the passage of electricity across a thin stratum of air; and therefore its production proves that electro-motion really occurred while the wires were yet separated by a thin stratum of air, which permitted the electric current to pass, and anterior to their actual contact.

The arrangement of figure 11, however, though good for establishing a principle, is not adapted for ordinary practice. The moist paper at *x* is a much less perfect conductor than a metal, and thus obstructs the passage of the current; nay, it does more, for it tends to establish an opposite current. In fact, on removing the dilute acid from *c*, and putting the zinc plate, *a*, in contact with

the plate of platinum, an ordinary simple circle would be formed, in which a positive current would flow from the zinc at x through the solution to and along the wire $x s b$. This current, in Faraday's experiment, was so feeble compared with the one excited by the acid solution, that its influence was scarcely appreciable; but if the opposed currents had been of the same force, no action would have ensued. To illustrate this still further, Faraday fixed a plate of platinum, r , figure 12, parallel and

Fig. 12.

near to a plate of amalgamated zinc, z . On placing a drop of dilute sulphuric acid at y , and making metallic contact between the plate at $z r$, a + current flowed in the direction of the arrows. If

Fig. 13.

in the same plates, fig. 13, the acid be introduced at x , and metallic contact made at $r z$, the current, passing as before from zinc through the liquid to the platinum, has a direction opposed to that of figure 2, owing to the reversed position of the acid. If, then, in the same plates, figure 14, a drop of acid be introduced at y and at x , the conditions are

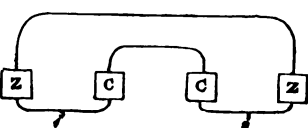
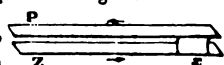
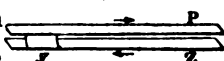
Fig. 14.

obviously fulfilled for producing two opposite currents of + electricity, each fluid acting as a substitute for metallic contact in conducting the current which the other tends to generate. If these opposing currents happen to be equal, they will annihilate the effects each separately would produce; and if unequal, the stronger current, as in figure 12, will annihilate the weaker, and, though with diminished power, impress its character on the circuit. A similar result occurs

Fig. 15.

when, as in figure 15, the order of one pair of plates is opposed to that of a second pair: the pair in bracket No. 1 sends a + current from left to right, and No. 2 from right to left; which currents, by means of the wire connecting the two copper plates, neutralize each other more or less completely according as they approach more or less to equality. This shows the effect of reversing the position of a pair of plates in a voltaic battery, and explains why oxidation should be confined to one only of the plates of which each pair consists.

To explain how chemical action excites electricity, recourse is had to the electro-chemical theory, first started by Davy in his essay on *Some Chemical Agencies of Electricity* (Phil. Trans. 1807). The views of Davy, which in some form or other have been adopt-



ed by most persons who have speculated on this subject, are founded on the assumption, now rendered so much more plausible than in his day, that electrical and chemical attractions are owing to one and the same agent. He considered chemical substances to be endowed with *natural electric energies*; meaning thereby, that a certain electric condition, either + or —, is natural to the atoms or combining molecules of bodies; that chemical union is the result of electrical attraction taking place between oppositely excited atoms, just as masses of matter when oppositely excited are mutually attracted; and that ordinary chemical decomposition arises from two combined atoms being drawn asunder by the electric energies of other atoms more potent than those by which they were united. Electro-chemical decomposition was at once explained by Davy on the same principles. He regarded the metallic terminations or *poles* of a voltaic circle (page 174) as two centres of electrical power, each acting repulsively to particles in the same electric state as itself, and by attraction on those which were oppositely excited. The necessary result was, that if the electric energy of the battery exceeded that by which the elements of any compound subject to its action were held together, decomposition followed, and each element was transferred bodily to the pole by which it was attracted, passing through solutions not containing the original compound, and refusing to unite with substances for which under other circumstances it would have combined. Substances which appeared at the + pole, such as oxygen, chlorine, and acids, were termed *electro-negative* substances; and those *electro-positive* bodies, which were separated at the — pole.

The views of Davy, both in his original essay and his subsequent explanations (Phil. Trans. 1826), were so generally and obscurely expressed, that chemists have never fully agreed, as to some points of the doctrine, about his real meaning. If he meant that a particle of free oxygen or free chlorine is in a negatively excited state, then his opinion is contrary to the fact, that neither of those gases affect an electrometer with — or any kind of electricity, any more than hydrogen gas or potassium alone exhibit any evidence of + excitement. If sulphur unites with oxygen because it has a + electric energy, why should it unite with potassium, which confessedly is far more + than itself? The only mode in which such facts as these seem reconcilable with the electro-chemical theory, is to suppose all bodies in their uncombined state to be electrically indifferent, but that they have a natural appetency to


assume one state in preference to another. Electro-negative bodies are such as assume negative excitement under a certain approximation to others which at the same time become positively excited, chemical union being the consequence. On this supposition, it is intelligible that sulphur may be + in relation to oxygen, and — to potassium, just as black silk is positively electrified by friction with sealing-wax, and negatively by white silk. Accordingly, *Bernardus*, and others who have since speculated on this subject, have been obliged to modify the theory as first given by *Davy*; and it is viewed at present in different ways by different persons. The following is what appears to me most correctly to harmonise with the laws of electricity and the phenomena to be explained:— A particle of zinc and a particle of oxygen, each possessed of + and — electricity, assume in combining opposite electric conditions, and combine, in consequence of such assumption, the particles adhering together by virtue of their opposite states, just as two oppositely excited pith balls are mutually attractive. The zinc particle in becoming + gives off — electricity to the mass of zinc or other body to which it had belonged; and, in like manner, the particle of oxygen, in becoming —, supplies + electricity to adjacent particles of oxygen or other adjacent substances. Thus electro-positive bodies in the act of combining give off — electricity, and electro-negatives set free + electricity. In general, these opposite electricities instantly neutralize each other; but under favourable circumstances, as in *Pouillet's* experiments, (page 119,) such effect is prevented. So, in an experiment by *De la Rive*, of transmitting dry chlorine gas mixed with air through an insulated copper tube, chloride of copper is generated: if the gases pass onward in a continuous current, the + electricity set free by the chlorine is carried off by the air, while the tube is rendered negative by the — electricity lost by those particles of copper which combine with the chlorine.

Chemical decomposition also excites electricity; and by this theory it ought to do so. For a particle of zinc in quitting oxygen is +, must recover — electricity before it can resume its natural state, and in doing so leaves contiguous substances +; and, similarly, the — oxygen renders objects — by robbing them of their + electricity. Hence, a body in combining excites in others an electric state opposite to that which it assumes; while in the act of decomposition it produces an effect exactly the reverse.

Again, it follows from the theory, that unless the zinc can as-

sume the + state by getting rid of — electricity, it cannot unite with oxygen; and that chemical union will more readily ensue, the more freely a conducting medium for carrying off such — electricity is supplied. This is applicable to Davy's method of preserving copper in sea-water (page 141). A piece of zinc in contact with copper corrodes rapidly by the copper carrying off its — electricity; while the copper thus constantly rendered —, is prevented from assuming the + state, and hence loses its power of uniting either with oxygen or chlorine. These principles readily apply to a simple voltaic arrangement, composed of zinc, copper, and dilute acid. In the broken circuit, the oxidation of the zinc causes the liquid, which supplies the oxygen, to be +; while the zinc plate is made — by the electricity given off by the oxidizing particle of zinc. This happens whether the copper plate is present or not. The + electricity diffused in the acid solution is in part taken up by the copper plate which thereby becomes +, and is in part lost by neutralizing the — electricity on the zinc plate. In the closed circuit, the — electricity on the zinc escapes along the conducting wire to the copper plate; the effect of which is, to promote the oxidation of the zinc on the principle above stated, and by rendering the copper —, to facilitate the extraction of + electricity from the liquid. A current of + electricity thus circulates from the zinc through the liquid to the copper, and of — electricity in the opposite direction (page 139). That plate which by chemical action with the liquid excites electricity, is called the *generating plate*; while the other is the *conducting plate*, because it performs the office of a conductor merely: in the common circle, zinc is the generating, and copper the conducting plate.

In a compound circle, represented by three pairs of plates, as in fig. 16, each pair of plates, indicated by the brackets, sends a current of + electricity from the zinc through the liquid to the

Fig. 16. The diagram shows three pairs of plates, each pair connected by a wire. The plates are labeled 'zinc' and 'copper' and are immersed in a 'fluid'. Arrows indicate the direction of current flow: from zinc to copper through the fluid, and from copper to zinc through the wire.

copper, rendering each copper plate +, while each zinc plate is —. The first copper and second zinc plates, being oppositely electrified, neutralize each other; and the same occurs with the second copper and third zinc, as with any number of plates similarly situated. The extreme plates alone can evince an electric state, the zinc in the broken circuit being —, and the copper +; and if these plates are connected by a wire, they, like the other zinc and copper plates of the series, neutralize each other, and a continuous current

is established through the whole battery, of + electricity in one direction, as shown by the arrows, and of — in the other. Thus, the quantity of electricity which circulates in one part of the closed battery, which is aptly called a *circle*, is, contrary to the notion of Volta, (page 180) the same in every part (page 150). The influence of a number of plates is to augment the intensity only (page 149). This subject has been ably discussed by De la Rive. (An. de Ch. et Ph. lxii. 180.)

Chemists are not agreed as to the order of electric energy in which the elements should be arranged. The following is that given by Bergelius, and may be viewed as approximative rather than rigidly exact :—Sulphur, nitrogen, and hydrogen scarcely occupy their true position in the series. The two former are less electro-negative than chlorine and fluorine, and hydrogen, I conceive, should occupy a prominent station among the electro-positive elements. All the bodies in the first series are — with regard to those in the second. In the first series each element is —, and in the second +, to all those which follow it.

1. *Negative Electrics*.—Oxygen, sulphur, nitrogen, chlorine, iodine, fluorine, phosphorus, silenium, arsenic, chromium, molybdenum, tungsten, boron, carbon, antimony, tellurium, columbium, titanium, silicon, osmium, hydrogen.

2. *Positive Electrics*.—Potassium, sodium, lithium, barium, strontium, calcium, magnesium, glucinium, yttrium, aluminium, zirconium, manganese, zinc, cadmium, iron, nickel, cobalt, cerium, lead, tin, bismuth, uranium, copper, silver, mercury, palladium, platinum, rhodium, iridium, gold.

Theory of Chemical Decomposition.—Compounds are decomposed by galvanism, so far as is known, only when they are more or less fluid, that state being apparently necessary for giving mobility to the elements, which are otherwise chained down to one spot and prevented from separating. Davy's opinion, that an element is actually transferred beyond the place in which the decomposing compound exists, is untenable after the experiments of Faraday (page 177). If a cell, AB, fig. 177, be filled with a solution of sulphate of soda, and a + current pass through it between the electrodes *b a* in the direction shown by the arrows, the sulphuric acid will appear at *b*, and the soda at *a*: but if AB be divided into three compartments *c, d, e*, by means of septa of moist bladder, *c, e*, and the sulphate of soda be confined to *d*, while dilute nitric acid be in *c* and *e*; then, the + current passing as before,

the sulphuric acid will be set free at the membrane *c*, and soda at *c*: not a particle of acid or alkali will go over to *a* or *b*; but the membranous septa will act as the electrodes or conveyers of the current into and from the solution of sulphate of soda, and at these septa only will the acid and alkali be set free. Should the solution soak through the bladder into *c* and *x*, then will the acid appear at *b*, and the alkali at *a*. In this, as in all similar cases, the elements of a compound are set free only when the current enters and quits the compound: acids, oxygen, and electro-negatives in general, appear at the electrode by which the + current enters; and alkalies, hydrogen, and electro-positives, whence the same current leaves the compound.

Facts like these are inconsistent with the hypothesis of Davy, by which he accounted for chemical decomposition and transfer, that attraction is exerted for the elements of compounds by the metallic conductors *a b*. The most feasible theory is that of Grothhus, of there being successive decompositions and recompositions in the line of particles lying between the electrodes. Let the upper part of fig. 18 represent a row of three particles of water lying between the electrodes *c z*, oxygen being represented by *o*, and hydrogen by \odot . A + current, in passing through them, is assumed to impart a kind of polar or magnetic virtue to the particles of oxygen and hydrogen, whereby affinity is weakened or destroyed on one side, and exalted on the other: each particle of hydrogen, for example, loses its attraction for the oxygen on its right side and quits it, but acquires an attraction for the oxygen on the left side and combines with it. Three particles of water thus yield, as in the lower part of fig. 18, two other particles are generated; while the extreme particles of oxygen and hydrogen are set free. There is thus no transfer from one spot to another; the oxygen and hydrogen are set free at the place where they pre-existed; and they are evolved as gases, unless, by some secondary action, they should unite with the matter of the electrodes or with some element of the solution.

This process of decomposition ensues quite independently of that chemical change by which the electric current is generated. Let *c z*, fig. 19, be a simple circle with platinum electrodes *p p'*, the liquid in the cells containing *c z* and *p p'* being dilute sulphuric acid, and a + current circulating as shown by the arrows. In the upper cell the want of affinity between the liquid and platinum

causes both gases to be evolved : that cell is one of *decomposition* merely ; but in the lower, the decomposition due to the electric current is compounded with that action between the zinc and liquid by which the electricity itself is generated. The lower cell is hence called a *generating cell*. Each generating cell of a battery, whether simple or compound, is also a decomposing one ; and the amount of decomposition in each, due to the current, is exactly the same as in a decomposing cell. The interposition of a decomposing cell retards the current, since the electricity has to overcome the affinity of the compound before it can circulate (page 179).

The preceding theoretical questions have been discussed on the assumption of electricity, as explained in the last section, being an independent principle susceptible of rapid motion from one body to another ; and that the condition of a voltaic conducting wire is similar to that of a wire leading from the ground to the prime conductor of an electrical machine, or which connects the inner and outer surface of a charged Leyden phial, except that the voltaic current moves slowly, owing to its lower tension and the interposed imperfect conductor. Some conceive that what is called an electric current is not an actual transfer of anything, but a process of induction among the molecules of a conductor passing progressively along it. Others, denying independent materiality to electricity, may ascribe it to a wave of vibrating matter, just as the phenomena of optics are explained by the undulatory theory. But whatever theory of the nature of electricity may be adopted, it seems necessary, after the experiments of Faraday on the identity of voltaic and common electricity, that the nature of an electric and voltaic current is essentially the same.

Fig. 17.

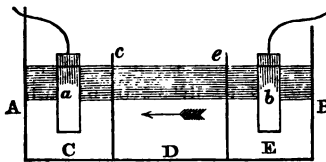


Fig. 18.

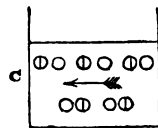
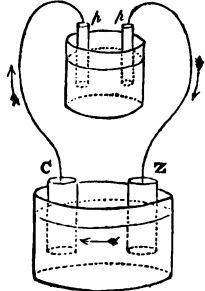


Fig. 19.



PART II.

INORGANIC CHEMISTRY.

PRELIMINARY REMARKS.

IN teaching a science such as chemistry, the details of which are numerous and complicated, it would be injudicious to follow the order of discovery, and proceed from individual facts to the conclusions which have been deduced from them. An opposite course is indispensable. It is necessary to discuss general principles in the first instance, in order to aid the beginner in remembering insulated facts, and in comprehending the explanations connected with them. The second part of this work will therefore commence with an explanation of the leading doctrines of the science. One inconvenience, indeed, arises from this method. It is often necessary, by way of illustration, to refer to facts of which the beginner is ignorant; and hence on some occasions more knowledge will be required for understanding a subject fully, than the reader may have at his command. But these instances will, it is hoped, be rarely met with; and when they do occur, the reader is advised to quit the point of difficulty, and return to the study of it when he shall have acquired more extensive knowledge of the details.

To the chemical history of each substance its chief physical characters will be added. A knowledge of these properties is not only advantageous in assisting the chemist to distinguish one body from another, but in many instances it is applied to uses still more important. The character called *specific gravity*, the meaning of which was explained at page 73, is of so much importance that the mode of determining it will be mentioned in this place. The process consists in weighing a body carefully, and then determining the weight of an equal bulk of water, the latter being regarded as unity. If, for example, a portion of water weigh nine grains, and the same bulk of another body 20 grains, its sp. gr. is determined by this formula;—as $9 : 20 :: 1$ (assumed as the sp. gr. of water)

to the fourth proportional 2.2222; so that the sp. gr. of any substance is found by dividing its weight by the weight of an equal volume of water. It is easy to discover the weight of equal bulks of water and any other liquid by filling a small bottle of known weight with each successively, and weighing them.* The method of obtaining the necessary data in case of a solid is somewhat different. The body is first weighed in air, is next suspended in water by means of a hair attached to the scale of the balance, and is then weighed again. The difference between the two weights gives the weight of a quantity of water equal to the bulk of the solid. This rule is founded on the hydrostatic law, that a solid body, immersed in any liquid, not only weighs less than it does in air, but the difference corresponds exactly to the weight of liquid which it displaces; and it is obvious that the liquid so displaced is exactly of the same dimensions as the solid. Another method is by the use of the bottle recommended for taking the sp. gr. of liquids. After weighing the bottle filled with water, a known weight of the solid is put into it, which of course displaces a quantity of water precisely equal to its own volume. The exact weight of the displaced water is found by weighing the bottle again, after its outer surface is made perfectly dry.

The determination of the sp. gr. of gaseous substances is an operation of much greater delicacy. From the extreme lightness of gases, it would be inconvenient to compare them with an equal bulk of water, and therefore atmospheric air is taken as the standard of comparison. The first step of the process is to ascertain the weight of a given volume of air. This is done by weighing a very light glass flask, furnished with a good stopcock, while full of air; and then weighing it a second time, after the air has been withdrawn by means of the air-pump. The difference between the two weights gives the information required. According to the observation of Prout, 100 cubic inches of pure and dry atmospheric air, at the temperature of 60° and when the barometer stands at 30 inches, weigh 31.0117 grains. By a similar method the weight of any other gas may be determined, and its sp. gr. be inferred accordingly. For instance, suppose 100 cubic inches of oxygen gas are found to weigh 34.109 grains, its sp. gr. will be thus deduced; as 31.0117 : 34.109 :: 1 (the sp. gr. of air) : 1.1025, the sp. gr. of oxygen.

* Bottles are prepared for this purpose by the philosophical instrument makers.

There are four circumstances to which particular attention must be paid in taking the specific gravity of gases :—

1. The gas should be perfectly pure, otherwise the result cannot be accurate.

2. Due regard must be had to its hygrometric condition. If it is saturated with moisture, the necessary correction may be made by the formula of page 77 ; or it may be tried by the use of substances which have a powerful attraction for moisture, such as chloride of calcium, quicklime, or fused potassa.

3. As the bulk of gaseous substances, owing to their elasticity and compressibility, is dependent on the pressure to which they are exposed, no two observations admit of comparison, unless made under the same elevation of the barometer. It is always understood, in taking the sp. gr. of a gas, that the barometer must stand at 30 inches, by which means the operator is certain that each gas is subject to equal degrees of compression. An elevation of thirty inches is called the standard height ; and if the mercurial column be not of that length at the time of performing the experiment, the error arising from this cause must be corrected by calculation. It has been established by experiment that the bulk of gases is inversely as the pressure to which they are subject. Thus, 100 measures of air, under the pressure of 30 inches of mercury, will dilate to 200 measures, if the pressure be diminished by one half ; and will be compressed to 50 measures, when the pressure is double, or equal to a mercurial column of 60 inches. The correction for the effect of pressure may therefore be made by the rule of three, as will appear by an example. If a certain portion of gas occupy the space of 100 measures at 29 inches of the barometer, its bulk at 30 inches may be obtained by the following proportion ; as $30 : 29 :: 100 : 96.66$.

It is understood that the temperature of the mercurial column is constant : if not so, correction must be made agreeably to the note at page 30.

4. For a similar reason the temperature should always be the same. The standard or mean temperature is 60° ; and if the gas be admitted into the weighing-flask when the thermometer is above or below that point, the formula of page 35 should be employed for making the necessary correction.

The first attempt to form a systematic chemical nomenclature was by Lavoisier, Berthollet, Guyton de Morveau, and Fourcroy, soon

after the discovery of oxygen gas. To avoid an undue use of new terms, the known elements and the more familiar compound bodies were allowed to retain the names which usage had assigned to them. The newly-discovered elements were named from some striking property. Thus, oxygen, from $\alpha\acute{\epsilon}\nu\varsigma$ acid, and $\gamma\epsilon\nu\nu\epsilon\iota\nu$ to generate, was so called from a belief that it is the universal cause of acidity; and the term hydrogen, from $\upsilon\delta\omega\rho$ water, and $\gamma\epsilon\nu\nu\epsilon\iota\nu$, was applied to the inflammable element of water. The compounds into which oxygen enters were termed *acids* or *oxides*, according as they do or do not possess acidity. The name of an acid was derived from the substance acidified by the oxygen, to which was added the termination in *ic*. Thus, sulphuric and carbonic acids signified compounds of sulphur and carbon with oxygen. Should sulphur or any other body form two acids, the name of that containing least oxygen was made to terminate in *ous*, as sulphurous acid. The termination in *uret* was applied to compounds of the simple non-metallic substances with each other, with a metal, or with a metallic oxide: thus, sulphuret and carburet of iron signify compounds of sulphur and carbon with iron. The general term *salt* comprehended compounds of acids with alkaline bases, and the names of the salts were so contrived as to indicate the substances contained in them. If the acid contain a maximum of oxygen, the name of the salt terminated in *ate*; if a minimum, the termination in *ite* was used: thus, sulphate and phosphate of potassa are salts of sulphuric and phosphoric acids; while the terms sulphite and phosphite of potassa denote salts of that alkaline with sulphurous and phosphorous acids.

These instances suffice to exhibit the principles by which the framers of the nomenclature were guided. Their object was to apply similar names to similar things, and so to construct those names as to indicate the nature or composition of the bodies to which they were attached. The same views have been acted on by succeeding chemists, who with this intention have availed themselves of the laws of definite combination. The more essential parts of this method, as adopted in these elements, are the following:—The names of newly-discovered elements are selected from some obvious property: thus, chlorine and iodine were so called from their colour. The termination of a name is rendered similar to those of nearly allied substances: thus, iodine and fluorine received that termination from their analogy to chlorine; the compounds of

chlorine, iodine, bromine, and fluorine, from their relations to oxygen, are termed *chlorides*, *iodides*, &c.; and the compounds of selenium, cyanogen, and other similar inflammables, are called *seleniurets*, *cyanurets*, &c. from their analogy to *sulphurets* and *phosphurets*. The names of metals, except some, as iron and tin, whose names have been sanctioned by usage, terminate in *um*, as potassium and titanium. The names of alkaline bases, when expressed by one word, terminate in *a*, as potassa and morphia. When one substance forms with oxygen three or more acids, a Greek preposition is usually prefixed to indicate the relative quantity of oxygen: thus, *hyponitrous* acid contains less oxygen than the nitrous; *hypernitrous* would apply to an acid with more oxygen than the nitrous; and *hyposulphuric* acid indicates an acid with less oxygen than the sulphuric, and more than the sulphurous. *Per* is sometimes prefixed with the same intention as *hyper*: thus, *perchloric* acid contains more oxygen than the chloric. Different oxides of the same metal are distinguished by derivatives from the Greek or Latin. An oxide consisting of an equivalent of each element is denoted either by the term oxide without any affix, or by *protoxide* (*πρωτος*, first); the highest grade is the *peroxide*; and the intermediate grades are distinguished by Latin numerals expressing the number of equivalents of oxygen combined with one equivalent of the metal, such as, *binoxide*, *teroxide*, &c. Sesquin, one and a half, is used to indicate the relation of 1 to $1\frac{1}{2}$, or 2 to 3, as in the Sesquin oxide of iron or cobalt. The Greek numerals *dis*, *tris*, *tetrahis*, are prefixed in like manner to denote oxides formed with one equivalent of oxygen, and two, three, or more equivalents of a metal. More complex ratios, such as 3oz. of a metal to 4oz. of oxygen, are denoted by a fraction, $\frac{4}{3}$, placed before the name of the oxide.

The same system is extended not merely to the union of elements generally with each other, but to compounds of a more complex nature, such as the salts. To a salt formed of an equivalent of the acid and alkali, its generic name without other addition is applied; but if two or more equivalents of the acid are attached to one oz. of the base, or two or more equivalents of the base to one oz. of the acid, a numeral is prefixed so as to indicate its composition. The two salts of sulphuric acid and potassa are called *sulphate* and *bisulphate*; the first containing an oz. of the acid and alkali, and the latter one oz. of the alkali to two of the acid. The three salts of oxalic acid and potassa are term-

ed the oxalate, *binoxalate*, and *quadroxalate* of potassa; because one oz. of the alkali is united with one oz. of acid in the first salt, with two in the second, and with three in the third. In the chromate and *dichromate* of oxide of lead, one oz. of the acid is united with 1 oz. of oxide in the former, and with two in the latter. The term salt has of late received considerable extension, being now applied to compounds analogous to common salts in constitution, though not formed of an acid and alkali. The grounds on which this has been done, and the nomenclature introduced in consequence, are explained in the section of the salts.—In speaking of salts of metallic oxides, many chemists are in the practice, for the sake of brevity, of mentioning the name of the metals only. Thus, in the expressions *sulphates of silver and lead*, the *oxide* of silver, and *oxide* of lead, are to be understood. The present comprehensive sense in which the word *salt* is used begins to render this practice objectionable.

The generic part of the name of a compound is usually formed from that ingredient which is considered the most highly electro-negative. Thus, to compounds of oxygen and chlorine, chlorine and iodine, iodine and sulphur, sulphur and potassium, in which the first of each pair is the electro-negative element, the correct appellations are *oxides* of chlorine, *chloride* of iodine, *iodide* of sulphur, *sulphuret* of potassium; and not *chloride* of oxygen, *iodide* of chlorine, *sulphuret* of iodine, and *potassiuret* of sulphur. This practice is invariably observed in this treatise.

Convenient and philosophical as this nomenclature may at first appear, its principles are now felt to be far from coextensive with the science. It much needs extension and modification. To many of the complex compounds known to chemists it is impracticable to apply convenient names correctly expressive of their constitution; and this has led to the use of those symbolic characters which have become general among chemists, and which are essential to the present state of chemistry. The mode of employing such notation will be explained in the second section of this part.

SECTION I.

AFFINITY.

ALL chemical phenomena are owing to Affinity or Chemical Attraction. It is the basis on which the science of chemistry is founded. It is, as it were, the instrument which the chemist employs in all his operations, and hence it forms the first and leading object of his study.

Affinity is exerted between the minutest particles of different kinds of matter, causing them to combine so as to form new bodies endowed with new properties. It acts only at insensible distances; in other words, apparent contact, or the closest proximity, is necessary to its action. Everything which prevents such contiguity is an obstacle to combination; and any force which increases the distance between particles already combined, tends to separate them permanently from each other. In the former case, they do not come within the sphere of their mutual attraction; in the latter, they are removed out of it. It follows, therefore, that though affinity is regarded as a specific power distinct from the other forces which act on matter, its action may be promoted, modified, or counteracted by them; and consequently, in studying the phenomena produced by affinity, it is necessary to inquire into the conditions that influence its operation.

The most simple instance of the exercise of chemical attraction is afforded by the admixture of two substances. Water and sulphuric acid, or water and alcohol, combine readily. On the contrary, water shows little disposition to unite with ether, and still less with oil; for, however intimately their particles may be mixed together, they are no sooner left at rest than the ether separates almost entirely from the water, and a total separation takes place between that fluid and the oil. Sugar dissolves very sparingly in alcohol, but to any extent in water; while camphor is dissolved in a very small degree by water, and abundantly by alcohol. It appears, from these examples, that chemical attraction is exerted between different bodies with different degrees of force. There is sometimes no proof of its existence at all: between some substances it acts very feebly, and between others with great energy.

Simple combination of two substances is a common occurrence ; of which the solution of salts in water, the combustion of phosphorus in oxygen gas, and the neutralization of a pure alkali by an acid, are instances. But the phenomena are often more complex. The formation of a new compound is often attended by the destruction of a pre-existing one ; as when some third body acts on a compound, for one element of which it has a greater affinity than they have for one another. Thus, oil has an affinity for the volatile alkali, ammonia, and will unite with it, forming a soapy substance called a liniment. But the ammonia has a still greater attraction for sulphuric acid ; and hence, if the acid be added to the liniment, the alkali will quit the oil, and unite by preference with the acid. If a solution of camphor in alcohol be poured into water, the camphor will be set free because the alcohol combines with the water. Sulphuric acid, in like manner, separates baryta from nitric acid. Combination and decomposition occur in each of these cases ;—combination of sulphuric acid with ammonia, of water with alcohol, of baryta with sulphuric acid ;—decomposition of the compounds formed of oil and ammonia, of alcohol and camphor, of nitric acid and baryta. These are examples of what Bergmann called *single elective affinity* ;—elective, because a substance manifests, as it were, a choice for one of two others, uniting with it by preference, and to the exclusion of the other. Many of the decompositions that occur in chemistry are instances of single elective affinity.

The order in which these decompositions take place has been expressed in tables ; of which the following, drawn up by Geoffroy, is an example :—

	<i>Sulphuric acid.</i>
	—
	Baryta,
	Strontia,
	Potassa,
	Soda,
	Lime,
	Ammonia,
	Magnesia,

This table signifies, first, that sulphuric acid has an affinity for the substances placed below the horizontal line, and may unite separately with each ; and, secondly, that the bases of the salts so formed will be separated from the acid by adding any of the alkalies or earths which stand above it in the column. Thus, ammonia will separate magnesia, lime ammonia, and potassa lime ; but none can withdraw baryta from sulphuric acid, nor can ammo-

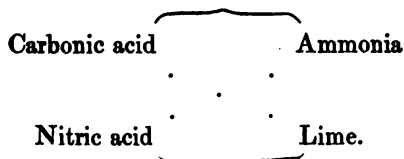
nia or magnesia decompose sulphate of lime, though strontia or baryta will do so. Bergmann conceived that these decompositions are solely determined by chemical attraction, and that consequently the order of decomposition represents the comparative forces of affinity; and this view, from the simple and natural explanation it affords of the phenomenon, was for a time very generally adopted. But Bergmann was in error. It does not necessarily follow, because lime separates ammonia from sulphuric acid, that the lime has a greater attraction for the acid than the volatile alkali. Other causes are in operation which modify the action of affinity to such a degree, that it is impossible to discover how much of the effect is owing to that power. It is conceivable that ammonia may in reality have a stronger attraction for sulphuric acid than lime, and yet that the latter, from the great influence of disturbing causes, may succeed in decomposing sulphate of ammonia.

The propriety of the foregoing remark will appear from the following example:—When a stream of hydrogen gas is passed over oxide of iron heated to redness, the oxide is reduced to the metallic state, and water is generated. On the contrary, when watery vapour is brought into contact with red-hot metallic iron, the oxygen of the water quits the hydrogen and combines with the iron. It follows from the result of the first experiment, according to Bergmann, that hydrogen has a stronger attraction than iron for oxygen; and from that of the second, that iron has a greater affinity for oxygen than hydrogen. But these inferences are incompatible with each other. The affinity of oxygen for the two elements, hydrogen and iron, must either be equal or unequal. If equal, the result of both experiments was determined by modifying circumstances; since neither of these substances ought on this supposition to take oxygen from the other. But if the forces are unequal, the decomposition in one of the experiments must have been determined by extraneous causes, in direct opposition to the tendency of affinity.

The fallacy of Bergmann's opinion was detected by Berthollet. He first showed that the relative forces of chemical attraction cannot always be determined by observing the order in which substances separate each other when in combination, and that the tables of Geoffroy are merely tables of decomposition, not of affinity. He likewise traced all the various circumstances that modify the action of affinity, and gave a consistent explanation of

the mode in which they operate. Berthollet went even a step further. He denied the existence of elective affinity as an invariable force, capable of effecting the perfect separation of one body from another, and maintained that all the instances of complete decomposition attributed to elective affinity are in reality determined by one or more of the collateral circumstances that influence its operation. But here this acute philosopher went too far. Bergmann erred in supposing the result of chemical action to be in every case owing to elective affinity; but Berthollet ran into the opposite extreme in declaring that the effects formerly ascribed to that power are never produced by it. That chemical attraction is exerted between bodies with different degrees of energy, is, I apprehend, indisputable. Water has a much greater affinity for hydrochloric acid and ammoniacal gases than carbonic and hydrosulphuric acids, and for these than for oxygen and hydrogen. The attraction of lead for oxygen is greater than that of silver for the same substance. The disposition of gold and silver to combine with mercury is greater than the attraction of platinum and iron for that fluid. As these differences cannot be accounted for by the operation of any modifying causes, we must admit a difference in the force of affinity in producing combination. It is equally clear that in some instances the separation of bodies from one another can only be explained on the same principle. No one, I conceive, will contend that the decomposition of hydriodic acid by chlorine, or of hydrosulphuric acid by iodine, is determined by the concurrence of any modifying circumstances.

Affinity is the cause of changes still more complicated than those which have just been considered. In a case of single elective affinity, three substances only are present, and two affinities are in play. But it frequently happens that two compounds are mixed together, and four different affinities brought into action. The changes that may or do occur under these circumstances may be studied by aid of a diagram. Thus, in mixing together a solution of carbonate of ammonia and nitrate of lime, their mutual action may be represented in the following manner:



Each of the acids has an attraction for both bases, and hence it is possible either that the two salts should continue as they were, or that an interchange of principles should ensue, giving rise to two new compounds,—carbonate of lime and nitrate of ammonia. According to the views of Bergmann, the result is solely dependant on the comparative strength of affinities. If the affinity of carbonic acid for ammonia, and of nitric acid for lime, exceed that of carbonic acid for lime, added to that of nitric acid for ammonia, then will the two salts experience no change whatever; but if the latter affinities preponderate, then, as does actually happen in the present example, both the original salts will be decomposed, and two new ones generated. Two decompositions and two combinations take place, being an instance of what is called *double elective affinity*. Kirwan applied the terms *quiescent* and *divellent* to denote the tendency of the opposing affinities,—the action of the former being to prevent a change, the latter to produce it.

The doctrine of double elective affinity was assailed by Berthollet on the same ground and with the same success as in the case of single elective attraction. He succeeded in proving that the effect cannot always be ascribed to the sole influence of affinity. For, to take the example already adduced, if carbonate of ammonia decompose nitrate of lime by the mere force of a superior attraction, it is manifest that carbonate of lime ought never to decompose nitrate of ammonia. But if these two salts are mixed in a dry state and exposed to heat, double decomposition does take place, carbonate of ammonia and nitrate of lime being formed; and therefore, if the change in the first example was produced by chemical attraction alone, that in the second must have occurred in direct opposition to that power. It does not follow, however, because the result is sometimes determined by modifying conditions, that it must always be so. I apprehend that the decomposition of the solid cyanuret of mercury by hydrosulphuric acid gas, which takes place even at a low temperature, cannot be ascribed to any other cause than a preponderance of the divellent over the quiescent affinities.

ON THE CHANGES THAT ACCOMPANY CHEMICAL ACTION.

The leading circumstance that characterises chemical action is the loss of properties experienced by the combining substances,

and the acquisition of new ones by the product of their combination. The change of property is sometimes inconsiderable. In a solution of sugar or salt in water, and in mixtures of water with alcohol or sulphuric acid, the compound retains so much of the character of its constituents, that there is no difficulty in recognising their presence. But more generally the properties of one or both of the combining bodies disappear entirely. One would not suppose from its appearance that water is a compound body; much less that it is composed of two gases, oxygen and hydrogen, neither of which, when uncombined, has ever been compressed into a liquid. Hydrogen is one of the most inflammable substances in nature, and yet water cannot be set on fire: oxygen, on the contrary, enables bodies to burn with great brilliancy, and yet water extinguishes combustion. The alkalies and earths were regarded as simple till Davy proved them to be compound; and certainly they evince no sign whatever of containing oxygen and a metal. Numerous examples of a similar kind are afforded by the mutual action of acids and alkalies. Sulphuric acid and potassa, for example, are highly caustic. The former is intensely sour, reddens the blue colour of vegetables, and has a strong affinity for alkaline substances; the latter has a pungent taste, converts the blue colour of vegetables to green, and combines readily with acids. On adding these principles cautiously to each other, a compound results called a *neutral salt*, which does not in any way affect the colouring matter of plants, and in which the other distinguishing features of the acid and alkali can no longer be perceived. They appear to have destroyed the properties of each other, and are hence said to *neutralize* one another.

The other phenomena that accompany chemical action are changes of density, temperature, form, and colour.

1. It is observed that two bodies rarely occupy, after combination, the same space which they possessed separately. In general their bulk is diminished, so that the sp. gr. of the new body is greater than the mean of its components. Thus a mixture of 100 measures of water and an equal quantity of sulphuric acid does not occupy the space of 200 measures, but considerably less. A similar contraction frequently attends the combination of solids. Gases often experience a remarkable condensation when they unite. The elements of olefiant gas, for instance, would expand to four times the bulk of that compound, if they were suddenly to become

free, and assume the gaseous form. But the rule is not without exception. The reverse happens in some metallic compounds; and there are examples of combination between gases without any change of bulk.

2. A change of temperature generally accompanies chemical action. Heat is evolved either when there is a diminution in the bulk of the combining substances without change of form, or when a gas is condensed into a liquid, or a liquid becomes solid. The heat caused by mixing sulphuric acid with water is an instance of the former; and the common process of slaking lime, during which water loses its liquid form in combining with that earth, is an example of the latter. The rise of temperature in these cases is obviously referable to diminished sp. heat in the new compound; but intense heat sometimes accompanies chemical action under circumstances in which an explanation founded on a change of sp. heat is inadmissible. At present it is enough to have stated the fact; its theory will be discussed under the subject of combustion. The production of cold seldom or never takes place during combination, except when heat is rendered insensible by the conversion of a solid into a liquid, or a liquid into a gas. All the frigorific mixtures act in this way.

3. The changes of form that attend chemical action are exceedingly various. The combination of gases may give rise to a liquid or a solid; solids sometimes become liquid, and liquids solid. Several familiar chemical phenomena, such as detonation, effervescence, and precipitation, are owing to these changes. The sudden evolution of a large quantity of gaseous matter causes an explosion, as when gunpowder detonates. The slower disengagement of gas produces effervescence, as when marble is put into hydrochloric acid. A precipitate is owing to the formation of a new body which happens to be insoluble in the liquid in which its elements were dissolved.

4. Chemical action is frequently attended by change of colour. No uniform relation has been traced between the colour of a compound and that of its elements. Iodine, whose vapour is of a violet hue, forms a beautiful red compound with mercury, and a yellow one with lead. The brown oxide of copper generally gives rise to green and blue coloured salts; while the salts of the oxide of lead, which is itself yellow, are for the most part colourless. The colour of precipitates is a very important

study, as it supplies a character by which most substances may be distinguished.

ON THE CIRCUMSTANCES THAT MODIFY AND INFLUENCE
THE OPERATION OF AFFINITY.

Of the conditions which are capable of promoting or counteracting the tendency of chemical attraction, the following are the most important: cohesion, elasticity, quantity of matter, gravity, and contact with other bodies. To these may be added the agency of the imponderables.

Cohesion.—The first obvious effect of cohesion is to oppose affinity, by impeding or preventing that mutual penetration and close proximity of the particles of different bodies, which is essential to the successful exercise of their attraction. Bodies seldom act chemically in their solid state; their molecules do not come within the sphere of attraction, and therefore combination cannot take place, although their affinity may in fact be considerable. Liquidity, on the contrary, favours chemical action; it permits the closest possible approximation, while the cohesive power is comparatively so trifling as to oppose no appreciable barrier to affinity.

Cohesion may be diminished in two ways, — by mechanical division, or by the application of heat. The former aids by increasing the extent of surface; but it is not of itself in general sufficient, because the particles, however minute, still retain that degree of cohesion which constitutes solidity. Heat acts with greater effect, and never fails in promoting combination, whenever the cohesive power is a barrier to it. Its intensity should always be so regulated as to produce liquefaction. The fluidity of one of the substances frequently suffices for effecting chemical union, as is proved by the facility with which water dissolves many salts and other solid bodies. But the cohesive force is still in operation; for a solid is commonly dissolved in greater quantity when its cohesion is diminished by heat. The reduction of both substances to the liquid state is the best method for ensuring chemical action. The slight degree of cohesion possessed by liquids does not appear to cause any impediment to combination; for they commonly act as energetically on each other at low temperatures, or at a temperature just sufficient to cause perfect liquefaction, as when their

cohesive power is still further diminished. It seems fair to infer, therefore, that very little, if any, affinity exists between two bodies which do not combine when they are intimately mixed in a liquid state.

The phenomena of crystallization are owing to the ascendancy of cohesion over affinity. When a large quantity of salt has been dissolved in water by the aid of heat, part of the saline matter generally separates as the solution cools, because the cohesive power of the salt then becomes comparatively too powerful for chemical attraction. Its particles begin to cohere together, and are deposited in crystals, the process of crystallization continuing till it is arrested by the affinity of the liquid. A similar change happens when a solution made in the cold is gradually evaporated. The cohesion of the saline particles is no longer counteracted by the affinity of the liquid, and the salt therefore assumes the solid form.

Cohesion plays a still more important part. It sometimes determines the result of chemical action, probably even in opposition to affinity. Thus, on mixing together a solution of two acids and one alkali, of which two salts may be formed, one soluble and the other insoluble, the alkali will unite with that acid with which it forms the insoluble compound, to the total exclusion of the other. This is one of the modifying circumstances employed by Berthollet to account for the phenomena of single elective attraction, and is certainly applicable to many of the instances to be found in the tables of affinity. When, for example, hydrochloric acid, sulphuric acid, and baryta are mixed together, sulphate of baryta is formed in consequence of its insolubility. Lime, which yields an insoluble salt with carbonic acid, separates that acid from ammonia, potassa, and soda, with all of which it makes soluble compounds.

A similar explanation may be given of many cases of double elective attraction. On mixing together in solution four substances, A, B, C, D, of which it is possible to form four compounds, AB and CD, or AC and BD, that compound will certainly be produced which happens to be insoluble. Thus, sulphuric acid, soda, nitric acid, and baryta may give rise either to sulphate of soda and nitrate of baryta, or to sulphate of baryta and nitrate of soda; but the first two salts cannot exist together in the same liquid, because the insoluble sulphate of baryta is instantly

generated, and its formation necessarily causes the nitric acid to combine with the soda. In like manner, a solution of nitrate of lime is decomposed by carbonate of ammonia, in consequence of the insolubility of carbonate of lime.

To comprehend the manner in which cohesion acts in these instances, it is necessary to consider what takes place when in the same liquid two or more compounds are brought together, which do not give rise to an insoluble substance. Thus, on mixing solutions of sulphate of potassa and nitrate of soda, no precipitate ensues; because the salts capable of being formed by double decomposition, sulphate of soda and nitrate of potassa, are likewise soluble. In this case it is possible either that each acid may be confined to one base, so as to constitute two neutral salts; or that each acid may be divided between both bases, yielding four neutral salts. It is difficult to decide this point in an unequivocal manner: but, judging from many chemical phenomena, there can, I apprehend, be no doubt that the arrangement last mentioned is the most frequent, and is probably universal whenever the relative forces of affinity are not very unequal. When two acids and two bases meet together in neutralizing proportion, it may therefore be inferred, that each acid unites with both the bases in a manner regulated by their respective forces of affinity, and that four salts are contained in solution. In like manner, the presence of three acids and three bases will give rise to nine salts; and when four of each are present, sixteen salts will be produced. This view affords the most plausible theory of the constitution of mineral waters, and of the products which they yield by evaporation.

The influence of insolubility in determining the result of chemical action may be readily explained on this principle. If nitric acid, sulphuric acid, and baryta are mixed together in solution, the base may be conceived to be at first divided between the two acids, and nitrate and sulphate of baryta to be generated. The latter, being insoluble, is instantly removed beyond the influence of the nitric acid, so that for an instant nitrate of baryta and free sulphuric acid remain in the liquid: but as the base left in solution is again divided between the two acids, a fresh quantity of the insoluble sulphate is generated; and this process of partition continues, until either the baryta or the sulphuric acid is withdrawn from the solution. Similar changes ensue when nitrate of baryta and sulphate of soda are mixed.

The separation of salts by crystallization from mineral waters or other saline mixtures is explicable by a similar mode of reasoning. Thus, on mixing nitrate of potassa and sulphate of soda, four salts, according to this view, are generated,—namely, the sulphates of soda and potassa, and the nitrates of those bases; and if the solution be allowed to evaporate gradually, a point at length arrives when the least soluble of these salts, the sulphate of potassa, will be disposed to crystallize. As soon as some of its crystals are deposited, and thus withdrawn from the influence of the other salts, the constituents of these undergo a new arrangement, whereby an additional quantity of sulphate of potassa is generated; and this process continues until the greater part of the sulphuric acid and potassa has combined, and the compound is removed by crystallization. If the difference in solubility is considerable, the separation of salts may be often rendered very complete by this method.

The efflorescence of a salt is sometimes attended with a similar result. If carbonate of soda and chloride of calcium are mingled together in solution, the insoluble carbonate of lime subsides. But if carbonate of lime and sea-salt are mixed in the solid state, and a certain degree of moisture is present, carbonate of soda and chloride of calcium are slowly generated; and since the former, as soon as it is formed, separates itself from the mixture by efflorescence, its production continues progressively. The efflorescence of carbonate of soda, which is sometimes seen on old walls, or which in some countries is found on the soil, appears to have originated in this manner.

Elasticity.—From the obstacle which cohesion puts in the way of affinity, the gaseous state, in which the cohesive power is wholly wanting, might be expected to be peculiarly favourable to chemical action. The reverse, however, is the fact. Bodies evince little disposition to unite when presented to each other in the elastic form. Combination does indeed sometimes take place, in consequence of a very energetic attraction; but examples of an opposite kind are much more common. Oxygen and hydrogen gases, and chlorine and hydrogen, though their mutual affinity is very powerful, may be preserved together for any length of time without combining. This want of action seems to arise from the distance between the particles preventing that close approximation which is so necessary to the successful exercise of affinity. Hence many

gases cannot be made to unite directly, which nevertheless combine readily while in their *nascent* state; that is, while in the act of assuming the gaseous form by the decomposition of some of their solid or fluid combinations.

Elasticity operates likewise as a decomposing agent. If two gases, the reciprocal attraction of which is feeble, suffer considerable condensation when they unite, the compound will be decomposed by very slight causes. Chloride of nitrogen, which is an oil-like liquid, composed of the two gases chlorine and nitrogen, affords an apt illustration of this principle, being distinguished for its remarkable facility of decomposition. Slight elevation of temperature, by increasing the natural elasticity of the two gases, or contact of substances which have an affinity for either of them, produces immediate explosion.

Many familiar phenomena of decomposition are owing to elasticity. All compounds that contain a volatile and a fixed principle are liable to be decomposed by a high temperature. The expansion occasioned by heat removes the elements of the compound to a greater distance from each other, and thus, by diminishing the force of chemical attraction, favours the tendency of the volatile principle to assume the form which is natural to it. The evaporation of water from a solution of salt is an instance of this kind.

Many solid substances which contain water in a state of intimate combination part with it in a strong heat, in consequence of the volatile nature of that liquid. The separation of oxygen from some metals, by heat alone, is explicable on the same principle.

From these and some preceding remarks, it appears that the influence of heat over affinity is variable; for at one time it promotes chemical union, and opposes it at another. Its action, however, is always consistent. Whenever the cohesive power is an obstacle to combination, heat favours affinity either by diminishing the cohesion of a solid, or by converting it into a liquid. As the cause of the gaseous state, on the contrary, it keeps at a distance particles which would otherwise unite; or, by producing expansion, it tends to separate from one another substances which are already combined. There is one effect of heat which seems somewhat anomalous; namely, the combination which ensues in gaseous explosive mixtures on the approach of flame. The expla-

nation given by Berthollet is probably correct,—that the sudden dilatation of the gases in the immediate vicinity of the flame acts as a violent compressing power to the contiguous portions, and thus brings them within the sphere of their attraction.

Some of the decompositions, which were attributed by Bergmann to the sole influence of elective affinity, may be ascribed to elasticity. If three substances are mixed together, two of which can form a compound which is less volatile than the third, the last will, in general, be completely driven off by the application of heat. The decomposition of the salts of ammonia by the pure alkalies or alkaline earths may be adduced as an example; and, for a like reason, all the carbonates are decomposed by nitric acid, and all the nitrates by sulphuric acid. This explanation applies equally well to some cases of double decomposition. It explains, for instance, why dry carbonate of lime will decompose nitrate of ammonia by the aid of heat; for carbonate of ammonia is more volatile than the nitrate either of ammonia or lime.

The influence of elasticity in determining the result of chemical action in these instances seems owing to the same cause which enables insolubility to be productive of similar effects. Thus, on mixing nitrate of ammonia with lime, the acid is divided between the two bases; some ammonia becomes free, which, in consequence of its elasticity, is entirely expelled by a gentle heat. The acid of the remaining nitrate of ammonia is again divided between the two bases; and if a sufficient quantity of lime is present, the ammoniacal salt will be completely decomposed. In like manner, the decomposition of potassa may be effected by iron, though the affinity of this metal for oxygen seems much inferior to that of potassium for oxygen. If potassa in the fused state be brought in contact with metallic iron at a white heat, the oxygen is divided between the two metals, and a portion of potassium set at liberty. But as potassium is volatile at a white heat, it is expelled at the instant of reduction; and thus, by its influence being withdrawn, an opportunity is given for the decomposition of an additional quantity of potassa.

Quantity of Matter.—The influence of quantity of matter over affinity is universally admitted. If one body, A, unites with another, B, in several proportions, that compound will be most difficult of decomposition which contains the smallest quantity of B. Of the three oxides of lead, for instance, the peroxide parts most

easily with its oxygen by the action of heat ; a higher temperature is required to decompose the red oxide ; and the protoxide will bear the strongest heat of our furnaces without losing a particle of its oxygen.

The influence of quantity over chemical attraction may be further illustrated by the phenomena of solution. When equal weights of a soluble salt are added in succession to a given quantity of water, which is capable of dissolving almost the whole of the salt employed, the first portion of the salt will disappear more readily than the second, the second than the third, the third than the fourth, and so on. The affinity of the water for the saline substance diminishes with each addition, till at last it is so weakened as to be unable to overcome the cohesion of the salt. The process then ceases, and a saturated solution results.

Quantity of matter is employed advantageously in many chemical operations. If a chemist wishes to displace a metallic oxide from an acid by the superior affinity of potassa for the latter, he frequently uses rather more of the alkali than is sufficient for neutralizing the acid. He employs an excess of the alkali, in order the more effectually to bring every particle of the substance to be decomposed in contact with the decomposing agent.

But Berthollet has attributed much greater influence to quantity of matter. It was the basis of his doctrine, developed in the *Statique Chimique*, that bodies cannot be wholly separated from each other by the affinity of a third substance for one element of a compound ; and to explain why a superior chemical attraction does not produce the effect which might be expected from it, he contended that quantity of matter compensates for a weaker affinity. From the co-operation of several disturbing causes, Berthollet perceived that the force of affinity cannot be estimated with certainty by observing the order of decomposition ; and he therefore had recourse to another method. He supposed the affinity of different acids for the same alkali to be in the inverse ratio of the ponderable quantity of each which is necessary for neutralizing equal quantities of the alkali. Thus, if two parts of one acid, A, and one part of another acid, B, are required to neutralize equal quantities of the alkali, C, it was inferred that the affinity of B for C was twice as great as that of A. He conceived, further, that as two parts of A produce the same neutralizing effect as one part of B, the attraction exerted by any alkali towards two parts of A ought to be precisely the

same as for the one part of B ; and he hence concluded that there is no reason why the alkali should prefer the small quantity of one to the large quantity of the other. On this he founded the principle that quantity of matter compensates for force of attraction.

Berthollet has here obviously confounded two things, namely, force of attraction and neutralizing power, which are really distinct. The relative weights of hydrochloric and sulphuric acids required to neutralize an equal quantity of any alkali, or, in other words, their capacities of saturation, are as 36·4 to 40, a ratio which remains constant with respect to all other alkalies. The affinity of these acids, according to Berthollet's rule, will be expressed by the same numbers. But in taking this estimate, we have to make three assumptions, each of which is disputable. There is no proof in the first place, that hydrochloric acid has a greater affinity for an alkali, such as potassa, than sulphuric acid. Such an inference would be directly opposed to the general opinion founded on the order of decomposition ; and though that order, as we have shown, is by no means a satisfactory test of the strength of affinity, it would be improper to adopt an opposite conclusion without having good reasons for so doing. Secondly, were it established that hydrochloric acid has the greater affinity, it does not follow that the attraction of those acids for potassa is in the ratio of 36·4 to 40. And, thirdly, supposing this point settled, it is very improbable that the ratio of their affinities for one alkali will apply to all others ; analogy would lead us to anticipate the reverse. Independently of these objections, Dulong has found that the principle of Berthollet is not in accord with the results of experiment.

Gravity.—The influence of gravity is perceptible when it is wished to make two substances unite, the densities of which are different. In a case of simple solution, a larger quantity of saline matter is found at the bottom than at the top of the liquid, unless the solution shall have been well mixed subsequently to its formation. In making an alloy of two metals which differ in density, a larger quantity of the heavier metal will be found at the lower than in the upper part of the compound, unless great care be taken to counteract the tendency of gravity by agitation. This force obviously acts, like the cohesive power, in preventing a sufficient degree of approximation.

Contact with other bodies.—The influence of contact of different substances in modifying affinity is observable either in the in-

creased or diminished energy of chemical action. The former is always the result of a galvanic current, and has been treated of elsewhere: the latter is produced by the interposition of an indifferent body by which others are removed out of the sphere of their mutual action. Thus, on immersing a fragment of pure zinc into dilute sulphuric acid the chemical action is no sooner commenced than it is checked by the hydrogen which is liberated; this is effected by the minute globules of the gas collecting upon the surface of the zinc, and adhering firmly to it, preventing the zinc and dilute acid from coming into that close contact, which is essential to chemical action. Some means must therefore be used to remove this intervening film of hydrogen, if a continuous action be desired: this is effected when the common zinc of commerce is used by the minute portions of other metals present in it as impurities, by which small but numerous galvanic currents are excited, and by their action the hydrogen is collected and makes its escape as globules of gas.

Imponderables.—The influence which heat exerts over chemical phenomena, and the modes in which it operates, have been already discussed. The chemical agency of galvanism has also been described. The effects of light will be most conveniently stated in other parts of the work. Electricity is frequently employed to produce the combination of gases with one another, and in some instances to separate them. It appears to act by the heat which it occasions, and therefore on the same principle as flame.

On the measure of affinity.—As the foregoing observations prove that the order of decomposition is not always a satisfactory measure of affinity, it becomes a question whether there are any means of determining the comparative forces of chemical attraction. When no disturbing causes operate, the phenomena of decomposition afford a sure criterion; but when the conclusions obtained in this way are doubtful, assistance may be frequently derived from other sources. The surest indications are procured by observing the tendency of different substances to unite with the same body under the same circumstances, and subsequently marking the comparative facility of decomposition when the compounds so formed are exposed to the same decomposing agent. Thus, on exposing silver, lead, and iron, to air and moisture, the iron soon rusts, the lead is oxidized in a slight degree only, and the silver resists oxidation altogether. Iron is hence inferred to have the greatest

affinity for oxygen, lead next, and silver the least. This conclusion is supported by concurring observations of a like nature, and confirmed by the circumstances under which the oxides of those metals part with their oxygen. Oxide of silver is reduced by heat only; and oxide of lead is decomposed by charcoal at a lower temperature than oxide of iron.

It is inferred from the action of heat on the carbonate of potassa, baryta, lime, and oxide of lead, that potassa has a stronger attraction for carbonic acid than baryta, baryta than lime, and lime than oxide of lead. The affinity of different substances for water may be determined in a similar manner.

Of all chemical substances, our knowledge of the relative degrees of attraction of acids and alkalies for each other is the most uncertain. Their mutual action is affected by so many circumstances, that it is in most cases impossible, with certainty, to refer any effect to its real cause. The only methods that have been hitherto devised for remedying this defect are those of Berthollet and Kirwan. Both are founded on the capacities of saturation, and the objections which have been urged to the rule suggested by the former philosopher apply equally to that proposed by the latter. But this uncertainty is of no great consequence in practice. We know perfectly the order of decomposition, whatever may be the actual forces by which it is effected.

SECTION II.

ON THE PROPORTIONS IN WHICH BODIES UNITE, AND ON THE LAWS OF COMBINATION.

THE study of the proportions in which bodies unite naturally resolves itself into two parts. The first includes compounds whose elements appear to unite in a great many proportions; the second comprehends those, the elements of which combine in a few proportions only.

I. The compounds contained in the first division are of two kinds. In one, combination takes place unlimitedly in all proportions; in the other, it occurs in every proportion within a certain limit. The union of water with alcohol and the liquid acids, such as the sulphuric, hydrochloric, and nitric, affords instances of

the first mode of combination ; the solutions of salts in water are examples of the second. One drop of sulphuric acid may be diffused through a gallon of water, or a drop of water through a gallon of the acid ; or they may be mixed together in any intermediate proportions ; and nevertheless in each case they appear to unite perfectly with each other. A hundred grains of water, on the contrary, will dissolve any quantity of sea-salt which does not exceed forty grains. Its solvent power then ceases, because the cohesion of the solid becomes comparatively too powerful for the force of affinity. The limit to combination is in such instances owing to the cohesive power ; and but for the obstacle which it occasions, the salt would most probably unite with water in every proportion.

All substances that unite in many proportions, give rise to compounds which have this common character, that their elements are united by a feeble affinity, and preserve, when combined, more or less of the properties which they possess in a separate state. In a scientific point of view, these combinations are of a minor importance ; but they are exceedingly useful as instruments of research. They enable the chemist to present bodies to each other, under circumstances peculiarly favourable for acting with effect : the liquid form is thus communicated to them ; while the affinity of the solvent or menstruum, which holds them in solution, is not sufficiently powerful to interfere with their mutual attraction.

II. The most interesting series of compounds is produced by substances which unite in a few proportions only ; and which, in combining, lose more or less completely the properties that distinguished them when separate. Of these bodies, some form but one combination. Thus there is only one compound of boron and oxygen, and of chlorine and hydrogen. Others combine in two proportions. For example, two compounds are formed by tin and oxygen, and by hydrogen and oxygen. Other bodies again unite in three, four, five, or even six proportions, which is the greatest number of compounds that any two substances are known to produce, except perhaps carbon and hydrogen, and those which belong to the first division.

The combination of substances that unite in a few proportions only, is regulated by the three following remarkable laws :—

1. The First of these Laws is, that the composition of bodies is fixed and invariable. A compound substance, so long as it

retains its characteristic properties, always consists of the same elements united together in the same proportion. Sulphuric acid, for example, is always composed of sulphur and oxygen in the ratio of 16 parts of the former to 24 of the latter: no other elements can form it, nor can it be produced by its own elements in any other proportion. Water, in like manner, is formed of 1 part of hydrogen and 8 of oxygen; and were these elements to unite in any other ratio, some new compound, different from water, would be the product. The same observation applies to all other substances, however complicated, and at whatever period they were produced. Thus sulphate of baryta, whether formed ages ago by the hand of nature, or quite recently by the operations of the chemist, is always composed of 40 parts of sulphuric acid and 76·7 of baryta. This law, in fact, is universal and permanent. Its importance is equally manifest: it is the essential basis of chemistry, without which the science itself could have no existence.

Two views have been proposed by way of accounting for this law. The explanation now universally given is confined to a mere statement, that substances are disposed to combine in those proportions to which they are so strictly limited, in preference to any others; it is regarded as an ultimate fact, because the phenomena are explicable on no other known principle. A different doctrine was advanced by Berthollet, in his *Statique Chimique*, published in 1803. Having observed the influence of cohesion and elasticity in modifying the action of affinity as already described, he thought he could trace the operations of the same causes in producing the effect at present under consideration. As the solubility of a salt and of a gas in water is limited, in the former by cohesion, in the latter by elasticity, he conceived that the same forces would account for the unchangeable composition of certain compounds. He maintained that within certain limits bodies have a tendency to unite in every proportion; and that combination is never definite and invariable, except when rendered so by the operation of modifying causes, such as cohesion, insolubility, elasticity, quantity of matter, and the like. Thus, according to Berthollet, sulphate of baryta is composed of 40 parts of sulphuric acid and 76·7 of baryta, not because those substances are disposed to unite in that ratio rather than in another, but because the compound so constituted happens to have great cohesive power.

These opinions were ably and successfully combated by Proust in several papers published in the *Journal de Physique*, wherein he proved that the metals are disposed to combine with oxygen and with sulphur only in one or two proportions, which are definite and invariable; and a controversy ensued remarkable for the moderation with which it was conducted on both sides. The question is now no longer at issue. The great variety of facts, similar to those observed by Proust, which have since been established, has proved beyond a doubt that the leading principle of Berthollet is erroneous. The tendency of bodies to unite in definite proportions only, is indeed so great as to excite a suspicion that all substances combine in this way; and that the exceptions thought to be afforded by the phenomena of solution, are rather apparent than real; for it is conceivable that the apparent variety of proportion, noticed in such cases, may arise from the mixture or combination of a few definite compounds with each other.

2. The Second Law of Combination is, that the relative quantities in which bodies unite, may be expressed by proportional numbers. Thus, 8 parts of oxygen united with 1 part of hydrogen, 16 of sulphur, 35.4 of chlorine, 39.6 of selenium, and 108 parts of silver. Such are the quantities of these five bodies which are disposed to unite with 8 parts of oxygen; and it is found that when they combine with one another, they unite either in the proportions expressed by those numbers, or in multiples of them according to the third law of combination. Hydrosulphuric acid, for instance, is composed of 1 part of hydrogen and 16 of sulphur, and bisulphuret of hydrogen of 1 part of hydrogen to 32 of sulphur; 35.4 of chlorine unite with 1 of hydrogen, 16 of sulphur, and 108 of silver; and 39.6 parts of selenium with 1 of hydrogen, and sixteen of sulphur.

From the occurrence of such proportional numbers has arisen the use of certain terms, as *Proportion*, *Combining Proportion*, *Proportional*, and *Chemical Equivalent* or *Equivalent*, to express them. The latter term, introduced by Wollaston, and which is employed in this treatise, was suggested by the circumstance that the combining proportion of one body is, as it were, *equivalent* to that of another body, and may be substituted for it in combination. Among the tables at the end of the volume will be found one of the equivalents of elementary substances.

This law is not confined to elementary substances, since compound

bodies have their combining proportions or equivalents, which may likewise be expressed in numbers. Thus, since water is composed of 1 eq. or 8 parts of oxygen, and 1 eq. or 1 of hydrogen, its combining proportion or equivalent is 9. The equivalent of sulphuric acid is 40, because it is a compound of one eq. or 16 parts of sulphur, and three eq. or 24 parts of oxygen; and in like manner, the eq. of hydrochloric acid is 36·4, because it is a compound of one eq. or 35·4 parts of chlorine, and one eq. or 1 part of hydrogen. The equivalent number of potassium is 39, and as that quantity combines with 8 of oxygen to form potassa, the equivalent of the latter is $39 + 8 = 47$. Now when these compounds unite, one equivalent of the one combines with one, two, three, or more equivalents of the other, precisely as the simple substances do. Hydrate of potassa, for example, is constituted of 47 parts of potassa and 9 of water, and its equivalent is consequently $47 + 9$, or 56. Sulphate of potassa is composed of 40 sulphuric acid + 47 potassa; and the nitrate of that alkali of 54 nitric acid + 47 of potassa. The equivalent of the former salt is therefore 87, and of the latter 101.

The composition of the salts affords a very instructive illustration of this subject; and to exemplify it still further, a list of the equivalents of a few acids and alkaline bases is annexed:—

Hydrofluoric Acid	19·7	Lithia	14
Phosphoric Acid	35·7	Magnesia	20·7
Hydrochloric	36·4	Lime	28·5
Sulphuric Acid	40·1	Soda	31·3
Nitric Acid	54·15	Potassa	47·15
Arsenic Acid	57·7	Strontia	51·8
Selenic Acid	63·6	Baryta	76·7

The alkalies are here shown to differ widely in neutralizing power; for the equivalent of each base expresses the quantity required to neutralize an equivalent of each of the acids. Thus 14 of lithia, 31·3 of soda, and 76·7 of baryta, combine with 54·15 of nitric acid, forming the neutral nitrates of lithia, soda, and baryta. The same fact is obvious with respect to the acids; for 40·1 of sulphuric, 54·15 of nitric, and 63·6 of selenic acid unite with 76·7 of Baryta, forming a neutral sulphate, nitrate and selenate of baryta.

These circumstances afford a ready explanation of a curious fact, first noticed by the Saxon chemist Wenzel; namely, that when two neutral salts mutually decompose each other, the resulting compounds are likewise neutral. The cause of this fact is now

obvious. If 71·3 parts of neutral sulphate of soda are mixed with 180·7 of nitrate of baryta, the 76·7 parts of baryta unite with 40 of sulphuric acid, and the 54 parts of nitric acid of the nitrate combine with the 31·3 of soda of the sulphate, not a particle of acid or alkali remaining in an uncombined condition.

Sulphate of Soda.		Nitrate of Baryta.	
Sulphuric acid	40	54	Nitric acid.
Soda	31·3	76·7	Baryta.
	<hr/> 71·3	<hr/> 130·7	

It matters not whether more or less than 71·3 parts of sulphate of soda are added ; for if more, a small quantity of sulphate of soda will remain in solution ; if less, nitrate of baryta will be in excess ; but in either case the neutrality will be unaffected.

3. The Third Law of combination is, that when one body, A, unites with another body, B, in two or more proportions, the quantities of the latter, united with the same quantity of the former, bear to each other a very simple ratio. The progress of chemical research, in discovering new compounds and ascertaining their exact composition, has shown that these ratios of B may be represented by one or other of the two following series :—

1st Series. A unites with 1, 2, 3, 4, 5, &c. of B.

2nd Series. A unites with 1, $1\frac{1}{2}$, 2, $2\frac{1}{2}$, &c. of B.

The first series is exemplified by the subjoined compounds.

Water is composed of	.	Hydrogen	1	.	Oxygen	8	} 1
Binoxide of Hydrogen	.	Do.	1	.	Do.	16	} 2
Carbonic Oxide	.	Carbon	6	.	Do.	8	} 1
Carbonic Acid	.	Do.	9	.	Do.	16	} 2
Nitrous Oxide	.	Nitrogen	14·15	.	Do.	8	} 1
Nitric Oxide	.	Do.	14·15	.	Do.	16	} 2
Hyponitrous Acid	.	Do.	14·15	.	Do.	24	} 3
Nitrous Acid	.	Do.	14·15	.	Do.	32	} 4
Nitric Acid	.	Do.	14·15	.	Do.	40	} 5

In all these compounds the ratio of the oxygen are expressed by whole numbers. In water the hydrogen is combined with half as much oxygen as in the binoxide of hydrogen, so that the ratio is as 1 to 2. The same relation holds in carbonic oxide and carbonic acid. The oxygen in the compounds of nitrogen and oxygen is in the ratio of 1, 2, 3, 4, and 5. In like manner the ratio of sulphur in the two sulphurets of mercury, and that of chlorine in the two chlorides of mercury, is as 1 to 2. So, in bicarbonate of potassa, the alkali is united with twice as much carbonic acid as

in the carbonate; and the acid of the three oxalates of potassa is in the ratio of 1, 2, and 4.

The following compounds exemplify the second series:—

Protoxide of Iron	consists of Iron	28	Oxygen	8	} 1
Peroxide	. . Do.	28	Do.	12	} $1\frac{1}{2}$
Protoxide of Manganese	. . Manganese	27.7	Do.	8	} 1
Sesqui-oxide	. . Do.	27.7	Do.	12	} $1\frac{1}{2}$
Bin-oxide	. . Do.	27.7	Do.	16	} 2
Arsenious Acid	. . Arsenic	37.7	Do.	12	} $1\frac{1}{2}$
Arsenic Acid	. . Do.	37.7	Do.	20	} $2\frac{1}{2}$
Hypophosphorous Acid	. . Phosphorus	15.7	Do.	4	} $\frac{1}{2}$
Phosphorous Acid	. . Do.	15.7	Do.	12	} $1\frac{1}{2}$
Phosphoric Acid	. . Do.	15.7	Do.	20	} $2\frac{1}{2}$

Both of these series, which together constitute the Third Law of Combination, result naturally from the operation of the second law. The first series arises from one equivalent of a body uniting with 1, 2, 3, or more equivalents of another body. The second series is a consequence of two equivalents of one substance combining with 3, 5, or more equivalents of another. Thus if two equivalents of phosphorus unite both with 3 and with 5 equivalents of oxygen, we obtain the ratio of $1\frac{1}{2}$ to $2\frac{1}{2}$; and should one equivalent of iron combine with one of oxygen, and another compound be formed of two equivalents of iron to three of oxygen, then the oxygen united with the same weight of iron would have the ratio, as in the table, of 1 to $1\frac{1}{2}$. The compounds of manganese and phosphorus with oxygen afford examples of the same nature. Still more complex arrangements will be readily conceived, such as 3 equivalents of one substance to 4, 5, or more of another. But it is remarkable that combinations of this kind are very rare; and even their existence, though theoretically possible, has not been decidedly established. Even some of the compounds which are usually included in the second series belong properly to the first. The red oxide of lead for instance, appears in its chemical relations not so much as a direct compound of lead and oxygen, but as a kind of salt formed by the union of the binoxide of lead with the protoxide of the same metal. On this supposition the two other oxides belong to the first series.

The merit of establishing the first law of combination seems due to Wenzel, a Saxon chemist; and the second law is deducible from his experiments on the composition of the salts. His work, entitled *Lehre der Verwandtschaft*, was published in 1777. Bergmann and Richter, a few years after, confirmed the observations

zel, though without adding materially in the way of generalization. Higgins in 1789 speculated on the atomic constitution of bodies in a manner which, if pursued, would have led to the discovery of Dalton. It is to the latter, science is indebted for deducing from the scattered facts which had been collected, a theory of chemical union, embracing the principles and giving it a consistency and form which before it was not possessed. In his hands the second law of combination attained its full generality; but the discovery, nearly his own, is that part of the third law of combination which is contained in the first of the two series above mentioned. The first public announcement of his views appears to have been made to the Philosophical Society of Manchester in 1803; and in 1808 they were explained in his *New System of Chemical Philosophy*. In the same year Wollaston and Thomson gave their evidence in support of the new doctrine, and other chemists have followed in the same path of inquiry. But of all who have successfully laboured in establishing the laws of combination, the most splendid contribution is that of the celebrated Berzelius. Struck with the perusal of the works of Richter, he commenced in 1807 an investigation into the *Laws of Definite Proportion*. Since that period his labours in this important field have been incessant, and every department of the science has been enriched by his skill and indefatigable industry. Whether we look to pneumatic chemistry, to the chemical history of the metals and of the salts, or to the composition of minerals, we are alike indebted to Berzelius. In all has he traced the laws of definite proportion, and by a multitude of exact analyses given to the laws of combination that certainty which accumulated facts can alone convey.

The utility of being acquainted with these important laws is manifest. Through their aid, and by remembering the equivalents of a few elementary substances, the composition of an extensive range of compound bodies may be calculated with facility. Thus, by knowing that 6 is the eq. of carbon and 8 of oxygen, it is easy to recollect the composition of carbonic oxide and carbonic acid; the first consisting of 6 parts of carbon + 8 of oxygen, and the second of 6 carbon + 16 of oxygen. The eq. of potassium is 39; and potassa, its protoxide, is composed of 39 of potassium + 8 of oxygen. From these few data, the composition of carbonate and

bi-carbonate of potassa are given; the former being composed of 22 parts of carbonic acid + 47 potassa, and the latter of 44 carbonic acid + 47 potassa. This method acts as an artificial memory, the advantage of which, compared with the former practice of stating the composition in 100 parts, will be manifest by inspecting the following quantities, and attempting to recollect them.

Carbonic Oxide.		Carbonic Acid.	
Carbon	42.86	.	27.27
Oxygen	57.14	.	72.73
Carbonate of Potassa.		Bi-carbonate of Potassa.	
Carbonic acid	31.43	.	47.83
Potassa	68.57	.	52.17

From the same data, calculations, which would otherwise be difficult or tedious, may be made rapidly and with ease, without reference to books, and frequently by a simple mental process. The exact quantities of substances required to produce a given effect may be determined with certainty, thus affording information which is often necessary to the success of chemical processes, and of great consequence both in the practice of the chemical arts, and in the operations of pharmacy.

The same knowledge affords a good test to the analyst by which he may judge of the accuracy of his result, and even sometimes correct an analysis which he has not the means of performing with rigid precision. Thus a powerful argument for the accuracy of an analysis is derived from the correspondence of its result with the laws of chemical union. On the contrary, if it form an exception to them, we are authorized to regard it as doubtful; and may hence be led to detect an error, the existence of which might not otherwise have been suspected. If an oxidized body be found to contain one equivalent of the combustible with 7.99 of oxygen, it is fair to infer that 8, or one equivalent of oxygen, would have been the result, had the analysis been perfect.

The composition of a substance may sometimes be determined by a calculation, founded on the laws of chemical union, before an analysis of it has been accomplished. When the new alkali lithia was first discovered, chemists did not possess it in sufficient quantity for determining its constitution analytically. But the neutral sulphates of the alkalies and alkaline earths are known to be composed of one equivalent of each constituent, and the oxides to contain one eq. of oxygen. If it be found, therefore, by analysis,

that neutral sulphate of lithia is composed of 40 parts of sulphuric acid and 14 of lithia, it may be inferred, since 40 is one eq. of the acid, that 14 is the eq. for lithia; and that this oxide is formed of 8 parts of oxygen and 6 of lithium.

The method of determining equivalent numbers will be anticipated from what has already been said. The commencement is made by carefully analyzing a definite compound of two simple substances which possess an extensive range of affinity. Thus water, a compound of oxygen and hydrogen, is found to contain 8 parts of the former to 1 of the latter; and if it be assumed that water consists of 1 eq. of oxygen and 1 of hydrogen, the relative weights of these equivalents will be as 8 to 1. The chemist then selects for analysis such compounds as he believes to contain 1 eq. of each element, in which either oxygen or hydrogen, but not both, is present. Carbonic oxide and hydro-sulphuric acid are suited to his purpose: as the former consists of 8 parts of oxygen and 6 of carbon, and the latter of 1 part of hydrogen and 16 of sulphur, the equivalent of carbon is inferred to be 6, and that of sulphur 16. The equivalent of all the other elements may be determined in a similar manner.

In researches on chemical equivalents there are two kinds of difficulty, one involved in the processes for ascertaining the exact composition of compounds, and the other in the selection of the compounds which contain single equivalents. Important general precautions in the experimental part of the subject are the following:—1, to exert scrupulous care about the purity of materials; 2, to select methods which consist of a few simple operations only; 3, to repeat experiments, and with materials prepared at different times; 4, to arrive at the same conclusion by two or more processes independent of each other. In the selection of compounds of single equivalents there are several circumstances calculated to direct the judgment:—

1. If two substances combine in several proportions, the law of multiples usually affects the electro-negative element of a compound. Thus, in the 5 compounds of nitrogen and oxygen, in which oxygen is the — element, 14 parts of nitrogen are united with 8, 16, 24, 32, and 40 parts of oxygen; whereas, taking the quantity of oxygen as constant, 8 parts of oxygen are united with 14, 7, 4.66, 3.5, and 2.8 parts of nitrogen, in which the simple ratio of the first series does not exist. This circumstance induces the chemist always to search among the oxides of the same element

for the lowest grade of oxidation, and in most cases to consider it as a compound of single equivalent. In some instances, however, the second degree of oxidation is formed of single equivalents, while the lowest oxide consists of 2 eq. of the + element and one of oxygen. Such compounds are called *dioxides* (page 193) and sometimes *suboxides*.

2. Metallic oxides, distinguished for strong alkalinity, or for acting as strong alkaline bases, are always protoxides. Dioxides rarely unite definitely with acids, and are remarkable for their ready conversion into protoxides with separation of metal. If the same metal yield several oxides, the protoxide is the strongest base; the highest grade of oxidation is frequently an acid, and the intermediate oxides are in general little distinguished either for alkalinity or acidity. Protoxides usually resist decomposition more obstinately than other oxides.

3. When a metal forms two oxides, the oxygen of which is in the ratio of 1 to $1\frac{1}{2}$, the first is usually the protoxide, and the second a compound of 2 eq. of the metal to three of oxygen. The oxides of iron and nickel are examples.

4. If two compounds resemble each other in their modes of combination, it is a strong presumption that their constitution is similar. Alumina and the peroxide of iron are remarkably allied in their chemical relations; and hence it is inferred, since the latter consists of 2 eq. of iron and 3 eq. of oxygen, that the former, whose composition would otherwise be very doubtful, is composed of 2 eq. of aluminium and 3 eq. of oxygen.

5. Mitscherlich has found, as is more fully stated in the article on crystallization, that certain compounds which resemble each other in composition and in their modes of combining, are likewise disposed in crystallizing to affect the same form. Hence it is a strong presumption that compounds which are analogous both in their crystalline figure and modes of combining, are also similar in their composition. In the oxide and acid of chromium the oxygen is in the ratio 1 to 2, and hence it was at first supposed that 1 eq. of chromium was united in the oxide with 1 eq. and in the acid with 2 eq. of oxygen. But the chromates resemble the sulphates in form and modes of combining, and the oxide of chromium bears the same analogy to alumina and peroxide of iron. The inference is, that oxide of chromium consists of 2 eq. of chromium and 3 eq. of oxygen, and chromic acid of 1 eq. of chromium and 3 eq. of oxygen.

6. Another guide in these inquiries is derived from the relation

traced by Dulong and Petit between the equivalents of a body and its sp. heat. The coincidences pointed out at page 55, are sufficiently numerous to show an interesting relation which is sometimes useful in selecting between doubtful numbers; but the instances of failure are at present too frequent to admit of this principle being used except with much caution.

7. The ready decomposition by galvanism, observed by Faraday, of compounds which consist of single equivalents, and the resistance to the same agent of many others not so constituted, promises to become an indication of great value in determining eq. numbers. The facts as yet known respecting it will be found in the section on galvanism.

8. Great light is often thrown on the chemical constitution of a compound by a knowledge of the *volumes* of the substances of which it is composed. This subject, however, will be discussed in an after part of this section.

Since the equivalents merely express the relative quantities of different substances which combine together, it is in itself immaterial what figures are employed to express them. The only essential point is, that the relation should be strictly observed. Thus, the eq. of hydrogen may be assumed as 10; but then oxygen must be 80, carbon 60, and sulphur 160. We may call hydrogen 100 or 1000; or, if it were desirable to perplex the subject as much as possible, some high uneven number might be selected, provided the due relation between the different numbers were faithfully preserved. But such a practice would destroy the advantage above ascribed to the use of equivalents; and it is the object of every one to employ such as are simple, that their relation may be perceived by mere inspection. Thomson makes oxygen 1, so that hydrogen is eight times less than unity, or 0.125, carbon 0.75, and sulphur 2. Wollaston, in his scale of chemical equivalents, estimated oxygen at 10; and hence hydrogen is 1.25, carbon 7.5, and so on. According to Berzelius, oxygen is 100. And lastly, several other chemists, such as Dalton, Davy, Henry, and others, selected hydrogen as their unit; and therefore the eq. of oxygen is 8. One of these series may easily be reduced to either of the others by an obvious and simple calculation. The numbers adopted in this work refer to hydrogen as unity, and are given in a table (Appendix in Table I.) constructed principally from the published tables of Berzelius, and partly from facts supplied by my own researches. The hypothesis that all equivalent numbers are simple multiples of the eq.

of hydrogen, has been elsewhere shown to be untenable. (Phil. Trans. 1833, Part ii. page 523.) Whenever the experimental quantity is nearly a whole number, the last may for many purposes be used as a sufficient approximation; and, accordingly, for such elements as carbon, sulphur, nitrogen, and potassium, which are often referred to in the way of illustration, I have generally adopted round numbers, as being shorter and more easily remembered than fractions. But on all occasions where exact calculations are concerned, the numbers given in the table should be employed.

The useful instrument known by the name of the *Scale of Chemical Equivalents*, was devised by Wollaston, and is a table of equivalents comprehending all those substances which are most frequently employed by chemists in the laboratory; and it only differs from other tabular arrangements of the same kind, in the numbers being attached to a sliding rule, which is divided according to the principle of that of Gunter. From the mathematical construction of the scale, it not only serves the same purpose as other tables of equivalents but in many instances supersedes the necessity of calculation. Thus, by inspecting the common table of equivalents we learn that 87 parts, or 1 eq. of sulphate of potassa contain 40 parts of sulphuric acid and 47 of potassa: but recourse must be had to calculation, when it is wished to determine the quantity of acid or alkali in any other quantity of the salt. This knowledge, on the contrary, is obtained directly by means of the scale of chemical equivalents. For example, on pushing up the slide until 100 marked upon it is in a line with the name sulphate of potassa on the fixed part of the scale, the numbers opposite to the terms sulphuric acid and potassa will give the precise quantity of each contained in 100 parts of the compound. In the original scale of Wollaston, for a particular account of which I may refer to the Philosophical Transactions for 1814, oxygen is taken as the standard of comparison; but hydrogen may be selected for that purpose with equal propriety, and scales of this kind have been prepared for sale by Reid of Edinburgh. A very complete scale of equivalents has been drawn up by Prideaux of Plymouth. (Phil. Mag. and Annals, viii. 430.)

ON THE ATOMIC THEORY.

The brief sketch which has been given of the laws of combination will, I trust, set in its true light the importance of that department of chemical science. It is founded on experiment alone, and

the laws which have been stated are the mere expression of fact. It is not necessarily connected with any speculation, and may be kept wholly free from it. The notion that the laws of combination involve something uncertain or hypothetical, is a fallacy easily referable to its source. It was impossible to reflect on the regularity and constancy with which bodies obey these laws, without speculating about the cause of that regularity; and, consequently, the facts themselves were no sooner noticed, than an attempt was made to explain them. Accordingly, when Dalton published his discovery of those laws, he at once incorporated the description of them with his notion of their physical cause, and even expressed the former in language suggested by the latter. Since that period, though several British chemists of eminence, and in particular Wollaston and Davy, recommended and practised an opposite course, both subjects have been too commonly comprised under the name of *atomic theory*; hence it has often happened that beginners have rejected the whole as hypothetical, because they could not satisfactorily distinguish those parts which are founded on fact from those which are conjectural. All such perplexity would have been avoided, and this department of the science have been far better understood, and its value more justly appreciated, had the discussion concerning the atomic constitution of bodies been always kept distinct from that of the phenomena which it is intended to explain. When employed in this limited sense, the atomic theory may be discussed in a few words.

Two opposite opinions have long existed concerning the ultimate elements of matter. It is supposed, according to one party, that every particle of matter, however small, may be divided into smaller portions, provided our instruments and organs were adapted to the operation. Their opponents contend, on the other hand, that matter is composed of certain ultimate particles or molecules, which by their nature are indivisible, and are hence termed *atoms* (from *α not*, and *τεμνω to cut*.) These opposite opinions have from time to time been keenly contested, and with variable success, according to the acuteness and ingenuity of their respective champions. But it was at last perceived that no positive data existed capable of deciding the question, and its interest therefore gradually declined. The progress of modern chemistry has revived attention to this controversy, by affording a far stronger argument in favour of the atomic constitution of matter than was ever advanced before, and

one which is almost irresistible. For the assumption that all bodies consist of ultimate atoms, the weight of which differs in different kinds of matter, supplies a luminous explanation of the laws of chemical union, which do not appear explicable on any other supposition.

According to the atomic theory, every compound is formed of the atoms of its constituents. An atom of A may unite with 1, 2, 3, or more atoms of B. Thus, supposing water to be composed of 1 atom of hydrogen and 1 atom of oxygen, binoxide of hydrogen will consist of 1 atom of hydrogen and 2 atoms of oxygen. If carbonic oxide is formed of 1 atom of carbon and 1 atom of oxygen, carbonic acid will consist of 1 atom of carbon and 2 atoms of oxygen. If, in the compounds of nitrogen and oxygen enumerated at page 217, the first or protoxide consist of 1 atom of nitrogen and 1 atom of oxygen, the four others will be regarded as compounds of 1 atom of nitrogen to 2, 3, 4, and 5 atoms of oxygen. From these instances it will appear, that the law of multiple proportion is a necessary consequence of the atomic theory. There is also no apparent reason why 2 or more atoms of 1 substance may not combine with 2, 3, 4, 5, or more atoms of another; but, on the contrary, these arrangements are necessary in explanation of the not unfrequent occurrence of half equivalents, as formerly stated. (Page 217.) Such combinations will also account for the complicated proportion noticed in certain compounds, especially in many of those belonging to the animal and vegetable kingdoms.

In consequence of the satisfactory explanation which the laws of chemical union receive by means of the atomic theory, it has become customary to employ the term *atom* in the same sense as combining proportion or equivalent. For example, instead of describing water as a compound of 1 eq. of oxygen and 1 eq. of hydrogen, it is said to consist of 1 atom of each element. In like manner sulphate of potassa is said to be formed of 1 atom of sulphuric acid and 1 atom of potassa, the word in this case denoting as it were a compound atom, that is, the smallest integral particle of the acid or alkali; a particle which does not admit of being divided, except by the separation of its elementary or constituent atoms. The numbers expressing the proportions in which bodies unite, must likewise indicate, consistently with this view, the relative weights of atoms; and accordingly these numbers are often called *atomic weights*. Thus, as water is composed of 8 parts of oxygen and 1 of hydrogen, it

follows, on the supposition of water consisting of 1 atom of each element, that an atom of oxygen must be 8 times heavier than an atom of hydrogen. If carbonic oxide be formed of an atom of carbon and an atom of oxygen, the relative weights of their atoms are as 6 to 8; and in short the chemical equivalents of all bodies may be considered as expressing the relative weights of their atoms.

The foregoing argument in favour of the atomic constitution of matter becomes much stronger when we trace the intimate connexion which subsists among many substances, between their crystalline form and chemical composition. This subject, however, now known under the name of *isomorphism*, will be more conveniently discussed under the head of crystallization.

Dalton supposes the atoms of bodies to be spherical; and he has invented certain symbols to represent the mode in which he conceives they may combine together, as illustrated by the following figures.

⊙ Hydrogen.
⊕ Nitrogen.

○ Oxygen.
● Carbon.

BINARY COMPOUNDS.

⊙○ Water.
○● Carbonic oxide.

TERNARY COMPOUNDS.

⊙⊙○ Binoxide of hydrogen.
⊙●○ Carbonic acid.
&c. &c. &c.

All substances containing only 2 atoms he called binary compounds, those composed of 3 atoms ternary compounds, of 4 quaternary, and so on.

There are several questions relative to the nature of atoms, most of which will perhaps never be decided. Of this nature are the questions which relate to the actual form, size, and weight of atoms, and to the circumstances in which they mutually differ. All that we know with any certainty is, that their weights do differ, and by exact analysis the relations between them may be determined. Peculiar views of the constitution of matter are held by Ampère, whose opinions are always acute and philosophical. He not only believes dissimilar atoms, as of oxygen and hydrogen, to be capable of uniting, but that 2 or more atoms of the same kind have a power of mutual attraction whereby they are arranged in groups of definite figure, which he calls *molecules*. These molecules more or

less intimately bound together by cohesion, give rise to the different states of bodies, the solid, liquid, and gaseous. Thus, oxygen gas is conceived not an assemblage of self-repulsive atoms of oxygen, but of molecules, each of which is a polyhedral solid made up of a constant number of atoms and repulsive to neighbouring molecules. In like manner he conceives the ultimate particles of compounds, as water and potassa, to be arranged in groups so as to constitute molecules. Similar views are maintained by Prout in his *Bridge-water Treatise*. This doctrine receives strong support from some phenomena of gaseous combination, and from the complex nature of organic compounds.

It is but justice to the memory of Higgins, to state that he first made use of the atomic hypothesis in chemical reasonings. In his "*Comparative View of the phlogistic and antiphlogistic Theories*," published in the year 1789, he observes (pages 36 and 37) that "in volatile vitriolic acid a single ultimate particle of sulphur is intimately united only to a single particle of dephlogisticated air; and that, in perfect vitriolic acid, every single particle of sulphur is united to 2 of dephlogisticated air, being the quantity necessary to saturation;" and he reasons in the same way concerning the constitution of water and the compounds of nitrogen and oxygen. These remarks of Higgins do not appear to have had the slightest connexion with the subsequent views of Dalton, who seems to have never seen the work of Higgins till after he had given an account of his own doctrine. The observations of Higgins, though highly creditable to his sagacity, do not affect Dalton's merit as an original observer. They were made, moreover, in so casual a manner, as not only not to have attracted the notice of his contemporaries, but to prove that Higgins himself attached no particular interest to them. Dalton's chief merit consists in having formed a complete theory of chemical union, and in the discovery of an essential and most important part of the doctrine, a merit which is solely and indisputably his; but in which he would have been anticipated by Higgins, had that chemist perceived the importance of his own opinions.

To the student who may desire a more ample account of the doctrine of atoms than the nature and limits of this volume admit of being given here, I may recommend a small work by Daubeny on the atomic theory, which in other respects will be found well worthy of perusal.

ON THE THEORY OF VOLUMES.

Soon after the publication of the New System of Chemical Philosophy in 1808, in which work Dalton explained his views of the atomic constitution of bodies, Gay-Lussac published in the *Memoires d'Arcueil* on the "Combination of Gaseous Substances with one another." He there proved that gases unite together by volume in very simple proportions, which he exemplified by the ratios in which the following gases unite:—

100 Hydrogen	.	to	.	50 Oxygen.
100 Ammoniacal	.	.	.	100 Hydrochloric acid gas.
100 do.	.	.	.	100 Fluoboric acid gas.
100 do.	.	.	.	200 do.
100 do.	.	.	.	100 Carbonic acid gas.
100 do.	.	.	.	200 do.

Various other examples were quoted, both from his own experiments and from those of others, all demonstrating the same fact. Thus ammonia was found by A. Berthollet to consist of 100 volumes of nitrogen gas and 300 volumes of hydrogen; sulphuric acid contains 100 volumes of sulphurous acid and 50 volumes of oxygen; and carbonic acid is formed by burning a mixture of 50 volumes of oxygen and 100 volumes of carbonic oxide.

From these and other instances Gay-Lussac established the fact, that gaseous substances unite in the simple ratio of 1 to 1, 1 to 2, 1 to 3, &c.; and this original observation has been confirmed by such a multiplicity of experiments, that it may be regarded as one of the best established laws in chemistry. Nor does it apply to gases merely, but to vapours also. For example, hydrosulphuric, sulphurous, and hydriodic acid gases are composed of

600 vol. hydrogen gas	and	100 vol. vapour of sulphur.
600 oxygen		100 sulphur.
100 hydrogen		100 iodine.

Another remarkable fact established by Gay-Lussac in the same essay is, that the volumes of compound gases and vapours always bear a very simple ratio to the volumes of their elements. This will appear from the following table, in which all the substances are supposed to be in the gaseous state:—

Volumes of Elements.			Volumes of resulting compounds.		
100 Nitrogen	+	300 Hydrogen	yield	200 Ammonia.	
50 Oxygen	+	100 Hydrogen	.	100 Water.	
50 Oxygen	+	100 Nitrogen	.	100 Protoxide of Nitrogen.	
100 Sulphur	+	600 Hydrogen	.	600 Hydrosulphuric acid.	
100 Sulphur	+	600 Oxygen	.	600 Sulphurous acid.	

Volumes of Elements.		Volumes of resulting Compounds.	
100 Chlorine	+	100 Hydrogen	yield 200 Hydrochloric acid.
100 Iodine	+	100 Hydrogen	. . . 200 Hydriodic acid.
100 Bromine	+	100 Hydrogen	. . . 200 Hydrobromic acid.
100 Cyanogen	+	100 Hydrogen	. . . 200 Hydrocyanic acid.
100 Oxygen	+	100 Nitrogen	. . . 200 Bin oxide of Nitrogen.

The law of multiples (page 217) is equally demonstrable by means of combining or eq. volumes as by combining or eq. weights. The annexed tabular view will justify this statement :—

Volumes of Elements.		Resulting Compounds.	
100 Nitrogen	+	50 Oxygen	yield Protoxide of Nitrogen.
100 do.	+	100 do.	. . . Bin oxide of Nitrogen.
100 do.	+	150 do.	. . . Hyponitrous acid.
100 do.	+	200 do.	. . . Nitrous acid.
100 do.	+	250 do.	. . . Nitric acid.
100 Hydrogen	+	50 do.	. . . Water.
100 do.	+	100 do.	. . . Bin oxide of Hydrogen.
100 Carbon Vapour	+	50 do.	. . . Carbonic oxide.
100 do.	+	100 do.	. . . Carbonic acid.

It thus appears that the laws of combination may equally well be deduced from the volumes as from the weights of the combining substances, and that the composition of gaseous bodies may be expressed as well by measure as weight. In the subjoined table is a comparative view of equivalent weights and volumes, to which is added the respective sp. gravities in relation both to air and hydrogen: the facts respecting the vapours are drawn from an essay by Mitscherlich. (An. de. Ch. et. Ph. lv. 5.) In constructing the table 100 volumes of hydrogen are assumed as the unit to which the eq. vol. of other substances are compared, and as the volume occupied by a weight of hydrogen represented by its equivalent. The eq. vol. of other substances, considered as gases, are in like manner the volumes corresponding to their equivalents taken as weights. In all substances, whose sp. gr. and equivalents are the same compared to the sp. gr. and eq. of hydrogen as unity, the eq. vol. is 100. If the sp. gr. is smaller than its equivalent, as in mercury, this must arise from its eq. vol. being proportionally greater than the eq. vol. of hydrogen; and if the sp. gr. is greater than its equivalent, as in oxygen or sulphur, the eq. vol. is proportionally smaller than the eq. vol. of hydrogen. A simple rule of three, therefore, enables the eq. vol. to be calculated. Thus the eq. vol. of mercury is $\frac{200}{196} \times 100 = 200$; that of oxygen $\frac{16}{32} \times 100 = 50$; and that of sulphur is $\frac{16 \cdot 10}{96 \cdot 48} \times 100 = 16 \cdot 66$, agreeably to the numbers which will be found in the table.

Gas and Vapours.	Specific Gravities.		Chemical Equivalents.	
	Air as 1.	Hydrogen as 1.	By Vol.	By Weight.
Hydrogen	0.0690	1.00	100	1.00
Nitrogen	0.9727	14.12	100	14.15
Chlorine	2.4700	35.84	100	35.42
Carbon (hypothetical)	0.4215	6.12	100	6.12
Iodine	8.7011	126.30	100	126.30
Bromine	5.3930	78.40	100	78.40
Water	0.6202	9.00	100	9.00
Alcohol	1.6012	23.24	100	23.25
Sulphuric Ether	2.5822	37.50	100	37.50
Light Carburetted Hydrogen	0.5595	8.12	100	8.12
Olefiant Gas	0.9810	14.24	100	14.24
Carbonic Oxide	0.9727	14.12	100	14.12
Carbonic Acid	1.5239	22.12	100	22.12
Protoxide of Nitrogen	1.5239	22.12	100	22.15
Sulphurous Acid	2.2105	32.10	100	32.10
Sulphuric Acid (anhydrous)	2.7617	40.10	100	40.10
Cyanogen	1.8157	26.35	100	26.35
Hydrosulphuric Acid	1.1770	17.10	100	17.10
Binoxide of Nitrogen	1.0377	15.06	200	30.15
Mercury	6.9690	101.00	200	202.00
Ammonia	0.5898	8.56	200	17.15
Hydrochloric Acid	1.2695	18.42	200	36.42
Hydriodic Acid	4.3850	63.63	200	127.26
Hydrobromic Acid	2.7310	39.71	200	79.40
Hydrocyanic Acid	0.9423	13.67	200	27.35
Arsenuretted Hydrogen	2.6950	39.20	200	78.20
Sesquichloride of Arsenic	6.2950	91.36	200	181.66
Sesquioxide of Arsenic	15.6400	227.00	200	454.28
Protochloride of Mercury	8.2040	119.00	200	237.42
Bichloride of Mercury	9.4390	137.00	200	272.84
Bromide of Mercury	9.6650	140.26	200	280.40
Bibromide of Mercury	12.3620	179.40	200	358.80
Biniodide of Mercury	15.6700	227.40	200	454.52
Oxygen	1.1025	16.00	50	8.00
Arsenious Acid	13.6695	198.4	50	99.40
Phosphorus	4.3273	62.8	25	15.70
Arsenic	10.3620	150.8	25	37.7
Sulphur	6.6480	96.48	16.66	16.10
Bisulphuret of Mercury	5.3840	78.10	33.33	234.18

The observations which more immediately flow from the facts in the preceding table are these :—

1. The combining or eq. volumes of substances, both elementary and compound, are either equal or have the simple ratio of 1 to 1, 1 to 2, 1 to 3, &c. The same simplicity rarely exists among the equivalent weights.

2. On comparing together the third and fifth columns, the corresponding numbers for the 18 first substances will be found nearly or quite identical. As those substances have the same uniting

volume as hydrogen, which is the assumed unit of comparison, and as the sp. gravities are merely the weights of equal volumes, the numbers of the third column, were they quite exact, must coincide with those in the fifth: their want of identity indicates errors of observation.

3. The identity in the eq. volumes of the elementary gases, hydrogen, nitrogen, and chlorine, led to the notion that the eq. volumes of most other elements, such as carbon, sulphur, and phosphorus, might also be identical. *Assuming* that identity, the sp. gravity which those elements ought to have when gaseous, may easily be calculated. Thus, taking 1, 6·12, and 16·1 as the equivalents of hydrogen, carbon, and sulphur, then will their sp. gravities in the gaseous state, eq. volumes being supposed equal, be in the ratio of 1, 6·12, and 16·1. This method, by which the hypothetical sp. gravity of carbon, as stated in the table, was obtained, was first indicated by Dr. Prout. (*An. of Phil.* vi. 321.) But though such hypothetical numbers may sometimes be used for the convenience of expressing the relation of uniting substances by measure, recent facts show how dangerous it would be to confide in them; for by the table it appears that the eq. volume of sulphurous vapour is one sixth of that of hydrogen, which renders the sp. gravity of the vapour of sulphur six times greater than the hypothetical number. Similar deviation is observable in phosphorus, arsenic, and mercury. In these cases, the real sp. gravity of a vapour is as much greater or less than the hypothetical as its eq. volume is less or greater than that of hydrogen.

4. The identity in the eq. volumes of hydrogen, nitrogen, and chlorine, suggested the idea that the atoms of all the elements are of the same magnitude; and this, coupled with the supposition that the self-repulsive energy of these atoms is equal, led to the opinion that equal volumes of the elements in the gaseous state must contain an equal number of atoms. This hypothesis, recommended by its simplicity, and supported by the fact that the volumes of gaseous substances vary according to the same law by varying temperature and pressure, was accordingly employed as a mode of determining the relative weights of atoms. As water consists of 50 measures of oxygen and 100 of hydrogen gas, it was inferred to be a compound of one atom of oxygen and two atoms of hydrogen; and consequently, taking 8 as the weight of an atom of oxygen, the weight of one atom of hydrogen is $\frac{1}{2}$ instead of 1, as in the table; or taking hydrogen

as 1, the atom of oxygen is 16. On the same principle may the numbers which in the table represent the eq. weights of chlorine, bromine, iodine, and nitrogen, which have the same eq. volumes as hydrogen, be considered as the weights of two equivalents. The equivalents adopted by Davy in his *Elements of Chemical Philosophy*, as well as those of Berzelius, which are now in general use on the Continent, were framed in accordance with these views: this the British chemist requires to bear in mind, since the same numbers which Berzelius uses for 2 eq. of hydrogen, nitrogen, chlorine, bromine, and iodine, he considers as one equivalent. But the opinion of Davy and Berzelius must now either be abandoned, or maintained on other principles, since the late researches of Dumas and Mitscherlich have shown experimentally that eq. volumes of the elementary gases and vapours do not contain the same number of atoms.

5. The facts contained in the last and preceding tables supply material for calculating the sp. gravity of compound gases, by which means the accuracy of other conclusions respecting their composition may be verified. This analysis proves that ammoniacal gas is composed of 100 volumes of nitrogen and 300 of hydrogen gases, condensed into the space of 200 volumes: if so, its sp. gravity will be

$$\frac{0.9727 + 3 \times 0.069}{2} = \frac{1.1797}{2} = 0.5889.$$

The near agreement of this calculated number with that found by weighing the gas itself, proves that ammonia has really the constitution above assigned to it, and gives great probability that the sp. gravity of nitrogen and hydrogen gases is nearly correct.

Again, hydrochloric acid gas consists of 100 volumes of hydrogen and 100 of chlorine gases united without any change of bulk, Hence its sp. gravity ought to be

$$\frac{2.47 + 0.069}{2} = 1.2695.$$

Hydrocyanic acid vapour is formed of 100 volumes of hydrogen and 100 of cyanogen gases united without change of volume; and therefore its sp. gravity should be

$$\frac{1.8157 + 0.069}{2} = 0.9423.$$

Considering olefiant gas as a compound of 200 volumes of hydrogen gas and 200 of the vapour of carbon condensed into 100, its sp. gravity will be $2 \times 0.069 + 2 \times 0.4215 = 0.1380 + 0.8430 = 0.9810$.

Aqueous vapour is composed of 100 volumes of hydrogen and 50 of oxygen gases condensed into the space of 100 volumes; and therefore its sp. gravity ought to be $0.069 + 0.5512$ (half the sp. gr. of oxygen) $= 0.6202$.

Protoxide of nitrogen is formed of 100 volumes of nitrogen and 50 of oxygen gases condensed into 100 volumes, and hence its sp. gravity should be $0.9727 + 0.5512 = 1.5239$.

Assuming carbonic oxide to be a compound of 100 volumes of carbon vapour and 50 of oxygen gas contracted in uniting into 100 volumes, its sp. gravity should be $0.4215 + 0.5512 = 0.9727$.

As the different sp. gravities thus calculated are very nearly those found by direct experiment, there is a strong presumption that the elements of the calculations are correct.

The principle of these calculations is sufficiently obvious. The sp. gravities represent the weights of equal volumes of the gases: taking 100 as the standard volume of which the sp. gravity of each gas denotes the weight, then 50 volumes of a gas may be indicated by half, 25 volumes by a fourth, and 16.66 by a sixth of its sp. gravity. Thus hydrosulphuric acid is a compound of 100 volumes of hydrogen gas, and 16.66 ($\frac{100}{6}$) of the vapour of sulphur condensed into 100 volumes, and therefore its sp. gravity is

$$0.069 + \frac{6.6480}{6} = 0.069 + 1.1080 = 1.1770.$$

Sulphurous acid consists of 100 volumes of oxygen gas and 16.66 of the vapour of sulphur condensed into 100 volumes; and hence its sp. gravity is

$$1.1025 + \frac{6.6480}{6} = 1.1025 + 1.1080 = 2.2105.$$

In these two gases the volume is the same as the hydrogen or oxygen which they contain, and therefore their sp. gravities are the sum of the weights of their elements. The same applies to water, protoxide of nitrogen, and carbonic oxide. In olefiant gas 400 volumes are condensed into 100, and therefore its sp. gravity is the sum of the sp. gravities of its elements. Hydrochloric acid gas occupies the same space as its elements, and therefore its sp. gravity

is found by taking the mean of their sp. gravities. The same remark applies to hydrocyanic acid. In ammonia 400 volumes are condensed into 200, and therefore the sum of the sp. gravities is halved.

As vapours are easily condensed by cold, and in many cases exist as such only at high temperatures, their sp. gravities may often be obtained by calculation more accurately than by experiment. Thus it is easier accurately to ascertain the sp. gravity of hydrogen and hydrosulphuric acid gases than of the vapour of sulphur; and therefore as soon as experiment has shown that the sp. gravity of that vapour is *somewhere about* 6.6480, then the precise number may be calculated. For as 100 volumes of hydrosulphuric acid gas contain 100 of hydrogen gas, the sp. gravity of the latter deducted from that of the former ($1.177 - 0.069$), gives 1.108 as the weight of combined sulphur. If the eq. volume of sulphur were 100, then must 1.108 be its sp. gravity; but as the number found experimentally is nearly six times 1.108, the inference is that the real sp. gravity is $6 \times 1.108 = 6.648$, and that its eq. volume is six times less than 100, or 16.66. The only assumption here is, that if the eq. volume of the vapour is not 100, it must be some multiple or submultiple of it by a whole number, consistently with the *theory of volumes*. In the construction of the preceding table I have given the sp. gravities of vapours calculated on these principles rather than the precise numbers given by experiment.

6. The volume of a compound gas in reference to the volumes of its components is determined by one of the following rules:

1. One volume of gas united with one volume, yield two volumes of the compound.

2. The volume of the compound gas often has the volume of that gas which enters most largely into it by volume.

3. The volume of the compound gas is equal to the sum of the volumes of its components divided generally by 2, but sometimes by 4 or 8.

4. In a few cases the sum of the component volumes must be divided by 3.

CHEMICAL SYMBOLS.

The impracticability in many cases of contriving convenient names expressive of the constitution of chemical compounds, especially of minerals, suggested the employment of symbols as an

abbreviated mode of denoting the composition of bodies. It was thought that the names of elementary substances, instead of being written at full length, might often be more conveniently indicated by the first letter of their names; and that the combination of elements with each other might be expressed by placing together, in some way to be agreed on, the letters which represent them. The advantage of such a symbolic language was felt so strongly by Berzelius, that he some years ago contrived a set of symbols, which he has since used extensively in his writings; and other eminent chemists as well as mineralogists, believing symbols to be useful, adopted those which Berzelius had proposed. The consequence is, that symbolic expressions, called *chemical formulæ*, are now so much resorted to, and are so identified with the language of chemistry, that essays of great value are in a measure as sealed books to those who cannot read symbols. It is therefore important that the chemical student, whatever he may think of the value of symbols, should not be unacquainted with them. Fortunately, the labour of a few minutes will enable him to understand the subject. The following table includes the symbols of all the elementary substances according to Berzelius.

TABLE OF SYMBOLS.

Elements.	Symb.	Elements.	Symb.	Elements.	Symb.
Aluminium .	Al	Gold (Aurum) .	Au	Potassium(Kalium)	K
Antimony(Stibium)	Sb	Hydrogen .	H	Rhodium .	R
Arsenic .	As	Iodine .	I	Selenium .	Se
Barium .	Ba	Iridium .	Ir	Silicon .	Si
Bismuth .	Bi	Iron (ferrum) .	Fe	Silver (Argentum)	Ag
Boron .	B	Lead (Plumbum)	Pb	Sodium (Natrium)	Na
Bromine .	Br	Lithium .	L	Strontium .	Sr
Cadmium .	Cd	Magnesium .	Mg	Sulphur .	S
Calcium .	Ca	Manganese .	Mn	Tellurium .	Te
Carbon .	C	Mercury (Hydrargyrum) .	Hg	Thorium .	Th
Cerium .	Ce	Molybdenum .	Mo	Tin (Stannum) .	Sn
Chlorine .	Cl	Nickel .	Ni	Titanium .	Ti
Chromium .	Cr	Nitrogen .	N	Tungsten (Wolfram) .	W
Cobalt .	Co	Osmium .	Os	Vanadium .	V
Columbium (Tantalum) .	Ta	Oxygen .	O	Uranium .	U
Copper (Cuprum)	Cu	Palladium .	Pd	Yttrium .	Y
Fluorine .	F	Phosphorus .	P	Zinc .	Zn
Glucinium .	G	Platinum .	Pl	Zirconium .	Zr.

For the sake of uniformity, and to prevent confusion, it is much to be wished that these symbols, being now generally known, should

be rigorously adhered to. Berzelius has properly selected them from Latin names, as being known to all civilized nations; and when the names of two or more elements begin with the same letter, the distinction is made by means of an additional letter.

The foregoing symbols are intended to represent the chemical eq. of the elements. Thus, the letters H, I, and Ba, stand for 1 eq. of hydrogen, iodine, and barium; and 2 H, 3 H, and 4 H, for 2, 3, and 4 eq. of hydrogen. Two eq. of an element are often denoted by placing a dash through or under its symbol: for instance, $\overline{\text{H}}$ or $\underline{\text{H}}$ means 2 H, and $\overline{\text{P}}$ or $\underline{\text{P}}$ signifies 2 P. Certain compounds are often, for the sake of brevity, denoted by single symbols in the same manner as the elements: thus an eq. of water, ammonia, and cyanogen, is sometimes expressed by Aq, Am, and Cy; but in general the formulæ for compound bodies are so contrived as to indicate the elements they contain, and the mode in which they are united. This may be done in several ways; but that which first suggests itself is, to connect together the symbols by the same signs as are used in Algebra. Thus the formulæ $\text{K} + \text{O}$, $\text{Ca} + \text{O}$, $\text{Ba} + \text{O}$, $\text{Mn} + \text{O}$, $\text{Fe} + \text{O}$, $2 \text{Fe} + 3 \text{O}$, $3 \text{H} + \text{N}$, $2 \text{H} + 2 \text{C}$, $\text{C} + 2 \text{O}$, $\text{N} + 5 \text{O}$, $\text{S} + 3 \text{O}$, and $\text{H} + \text{Cl}$, denote single eq. of potassa, lime, baryta, protoxide of manganese, protoxide of iron, peroxide of iron, ammonia, olefiant gas, carbonic acid, nitric acid, sulphuric acid, and hydrochloric acid. The formula $\text{K} + \text{N} + 6 \text{O}$ indicates the elements which are contained in an eq. of nitrate of potassa: in order to express further that the potassium is combined with only 1 eq. of oxygen, the remaining oxygen with the nitrogen, and the potassa with nitric acid, the symbols are placed thus, $(\text{K} + \text{O}) + (\text{N} + 5 \text{O})$, the brackets containing the symbols of those elements which are supposed to be united. A number placed on the outside of a bracket multiplies the compound within it: thus $(\text{K} + \text{O}) + (\text{S} + 3 \text{O})$ is sulphate of potassa, and $(\text{K} + \text{O}) + 2(\text{S} + 3 \text{O})$ is the bisulphate. All the elements contained in a compound are thus visibly represented, and the chemist is able readily to trace all possible modes of combination, and to select that which is most in harmony with the facts and principles of his science. He may, and often does, thereby detect relations which might otherwise have escaped notice.

Another advantage attributable to such formulæ is, that they facilitate the comprehension of chemical changes. If hydro-sulphuric acid acts upon the protoxide of lead, it is easy to say that

the sulphur combines with the lead and the hydrogen with the oxygen; but the exact adaptation of the quantities for mutual interchange appears to me more clearly shown by symbols than by a description or a diagram, both of which are apt to produce confusion where the change to be explained is complex. In the simple instance alluded to, $H + S$ reacts on $Pb + O$, and the products are $Pb + S$ and $H + O$. When hydrosulphuric acid acts on bichcyanuret of mercury, the result is bisulphuret of mercury and hydrocyanic acid: the substances which interchange elements are $2(H + S)$ and $Hg + 2Cy$; and the products are $Hg + 2S$, and $2(H + Cy)$. In more complicated changes the advantage of chemical formulæ is still more manifest, examples of which kind will be found in the section on cyanogen, and in other parts of this volume.

Useful as the algebraic chemical formulæ are for the purpose of studying chemical changes, they are sometimes found inconveniently long where the object is merely to express the composition of bodies, and accordingly Berzelius has introduced several abbreviations. For instance, he indicates degrees of oxidation by dots placed over the symbol, writing $\overset{\cdot}{K}$, $\overset{\cdot\cdot}{C}$, $\overset{\cdot\cdot\cdot}{N}$, instead of $K + O$, $C + 2O$, $N + 5O$, for potassa, carbonic acid, and nitric acid. In like manner he denotes compounds of sulphur by commas, writing $\overset{\cdot}{K}$, $\overset{\cdot\cdot}{Hg}$, $\overset{\cdot}{H}$ instead of $K + S$, $Hg + 2S$, $H + S$, for sulphuret of potassium, bisulphuret of mercury, and hydrosulphuric acid. When the ratio is that of 2 to 3 he employs the symbol for two eq. above stated: thus, $\overset{\cdot\cdot\cdot}{Fe}$, $\overset{\cdot\cdot}{P}$, $\overset{\cdot\cdot\cdot}{As}$, is used instead of $2Fe + 3O$, $2P + 5O$, $2As + 5O$, for an equivalent of peroxide of iron, phosphoric acid, and arsenic acid; and similarly we have $\overset{\cdot\cdot\cdot}{As}$, $\overset{\cdot\cdot}{As}$, instead of $2As + 3S$, $2As + 5S$ for the sesquisulphuret and persulphuret of arsenic. These last formulæ are sometimes used to indicate two eq. instead of one; but as, agreeably to the atomic theory, the smallest possible particle of peroxide of iron consists of 2 atoms of iron and 3 of oxygen, the formula $2Fe + 3O$ ought to stand for 1 eq. only.

Berzelius often dispenses with the sign +, and writes combined elements side by side, the sign of addition being understood instead of expressed. Thus he uses HO , KO , FeS , $Ca\overset{\cdot\cdot}{C}$, $Ba\overset{\cdot\cdot\cdot}{N}$, $\overset{\cdot\cdot\cdot}{K}\overset{\cdot\cdot\cdot}{S} + \overset{\cdot\cdot\cdot}{Ni}\overset{\cdot\cdot\cdot}{S}$, instead of $H + O$, $K + O$, $Fe + S$, $Ca + \overset{\cdot\cdot}{C}$,

$\text{Ba} + \ddot{\text{N}}, (\dot{\text{K}} + \ddot{\text{S}}) + (\ddot{\text{Ni}} + \ddot{\text{S}})$, for water, potassa, sulphuret of iron, carbonate of lime, nitrate of baryta, and the double sulphate of potassa and oxide of nickel. Two or more equivalents of one constituent of a compound are denoted by numbers placed in the same position as the indices of powers in algebra: thus

NH^3 , NC^2 , $\ddot{\text{Fe}}^2$, $\dot{\text{H}}^3$, is the abbreviation of $\text{N} + 3\text{H}$, $\text{N} + 2\text{C}$,

$2\ddot{\text{Fe}}$, $+ 3\dot{\text{H}}$ for ammonia, cyanogen, and sesquihydrate of iron, a compound of 2 eq. of peroxide of iron and 3 of water. A number used before symbols, like coefficients in algebra, multiplies all the following symbols not separated from it by a + sign. Thus in

$8 \text{Ca} \ddot{\text{Si}} + \dot{\text{K}} \ddot{\text{S}}^2 + 16 \text{aq.}$ (which is the formula for the mineral called apophyllite) the 8 denotes 8 eq. of $\text{Ca} \ddot{\text{Si}}$, or silicate of lime, which are united with 1 eq. of bisilicate of potassa, and 16 of water.

Berzelius also expresses the vegetable and animal acids by the first letter of their name, with a dash over it. Thus $\overline{\text{T}}$, $\overline{\text{A}}$, $\overline{\text{C}}$, $\overline{\text{B}}$, $\overline{\text{G}}$, $\overline{\text{F}}$, are the symbols for tartaric, acetic, citric, benzoic, gallic, and formic acids.

Several objections, some of which are of great weight, have been made to this system of symbols, and various modifications have been proposed by different authors. Among these, that which has been adopted by Liebig and Poggendorff in their chemical dictionary, combine more successfully than any other the requisite clearness, brevity, and generality, and will be used in this work. The changes which have been made will readily be seen by comparing the accompanying symbols of apophyllite $8 (\text{Ca O}, \text{SiO}_3) + \text{KO}, 2\text{SiO}_3 + 16 \text{aq.}$ with that of Berzelius for the same mineral. From this example it will be observed that this system of symbols is based upon the following principles:—that the numbers a little below and to the right of the symbols, effect those only to which they are immediately attached, while those which are written before the symbol effect all that follow as far as the next full stop or sign of addition; if a figure be placed before a parenthesis it applies to all contained within it. Owing to these various abbreviations the same compound may be written in different ways. Thus the constitution

of a crystal of alum is represented by $\dot{\text{K}} \ddot{\text{S}} + \ddot{\text{Al}} \ddot{\text{S}}^3 + 24 \dot{\text{H}}$, or $\text{KO}, \text{SO}_3 + \text{Al}_2 \text{O}_3, 3\text{SO}_3 + 24 \text{aq.}$ This certainly tends to confuse a beginner; but the methods are so simple that a very

little practice, guided by the numerous examples dispersed through these pages, will remove all difficulty.

The symbol aq. which has been used for water instead of HO, or \dot{H} requires particular attention. Many substances in crystallizing from an aqueous solution combine during the act of solidification with a definite quantity of water, which, from being essential to the existence of the crystal, has been called the water of crystallization. This water is but feebly retained, the compound frequently undergoing spontaneous decomposition, and never withstanding a moderate increase of temperature, or exposure to a diminished atmospheric pressure, the crystal at the same time losing its transparency and frequently falling into powder. In other cases the compounds containing water are much more permanent, and may exist either in the gaseous, liquid, or solid state: these compounds are called hydrates. For the purpose of distinguishing water in different states of combination, Liebig and Poggendorff propose to express water of crystallization by aq. while hydratic water is denoted by an h attached to the symbol of the substance containing it. Thus \overline{A} being the symbol of acetic acid, \overline{A}_h is the symbol of the hydrate: similarly the symbol M_gO , $\overline{M}_h + 4 \text{ aq.}$ denotes the malate of magnesia and five eq. of water, but distinguishes four of these as water of crystallization, while the fifth is united with the malic acid and forms with it a hydrate. The symbol HO is used in doubtful cases, and when changes effected by chemical action are explained.

ISOMERIC BODIES.

It was formerly thought that the same elements united in the same ratio must always give rise to the same compound; but within these few years several examples have been discovered of two or even more substances containing the same elements in the same ratio, and yet exhibiting chemical properties distinct from each other. For such compounds Berzelius has suggested the general appellation of *isomeric*, from *ισος* equal, and *μερος* part, expressive of equality in the ingredients. Interesting instances of this kind are the two cyanic acids, which consist of cyanogen and oxygen in the same ratio, and have the same equivalent, yet differ widely in their chemical properties; and a similar example is afforded by the tartaric and paratartaric acids. Para from *παρα* near to, is prefixed in order to mark the relation to tartaric acid, a principle of nomenclature which is extended to other cases.

Unexpected as was the discovery of isomerism, it is quite consistent with our theories of chemical union, insomuch as the same elements may be grouped or combined in different ways, and thereby give rise to compounds essentially distinct. Thus the elements of sulphate of potassa may perhaps be united indiscriminately with each other, as expressed by the formula KSO_4 ; or they may form $\text{KO} + \text{SO}_3$; or $\text{KS} + \text{O}_4$; or $\text{KO}_2 + \text{SO}_2$; and other combinations might be made. The second of these is thought to be the real one; but no one can say that the others are impracticable. Again, the elements of peroxide of tin, Sn and 2O , may either form SnO_2 , or $\text{SnO} + \text{O}$; and those of the peroxide of iron, 2Fe and 3O , may either be Fe_2O_3 , or $\text{FeO} + \text{FeO}_2$, not to mention other possible combinations. The elements of alcohol are 4C , 6H , and 2O , which may be united indiscriminately as $\text{H}_6\text{C}_4\text{O}_2$, $\text{H}_6\text{C}_4 + 2\text{O}$, $\text{H}_5\text{C}_4\text{O} + \text{HO}$, or $\text{H}_4\text{C}_4 + 2\text{HO}$, besides others.

Some bodies consist of the same elements in the same ratio, and yet differ in their equivalents. A marked example is supplied by olefiant gas and etherine, the former of which contains 200 volumes of carbon vapour and 200 of hydrogen gas condensed into 100 volumes, and the latter of 400 volumes of carbon vapour and 400 of hydrogen gas, united so as to yield 100 volumes of etherine. The equivalent of olefiant gas is $14\cdot24$, and that of etherine $28\cdot48$, or exactly double. A similar case will be found in the description of cyanuric acid. The nature of these compounds is at once detected by their equivalents being unlike, and by the volume which they occupy as gases compared with the volumes of the elements of which they consist. Isomeric bodies of this kind are obviously much less intimately allied than those above described.

SECTION III.

OXYGEN.

History.—Discovered by Priestley in 1774, and by Scheele a year or two after, without previous knowledge of Priestley's discovery. It was termed *Dephlogisticated air* by Priestley, *Empyreal air* by Scheele, and *Vital air* by Condorcet. The name it now bears, derived from the Greek words $\alpha\acute{\kappa}\omega\varsigma$ *acid* and $\gamma\epsilon\gamma\eta\mu\epsilon\iota\upsilon$ *to generate*, was proposed by Lavoisier, who considered it the sole cause of acidity.

Preparation.—From several sources, the peroxides of manganese, lead, and mercury, nitre, and chlorate of potassa, yield it in large quantities when they are exposed to a red heat. The substances commonly employed for the purpose are peroxide of manganese and chlorate of potassa. It may be procured from the former in two ways; either by heating it to redness in a gun-barrel, or in a retort of iron or earthenware; or by putting it in fine powder into a flask with about an equal weight of concentrated sulphuric acid, and heating the mixture by means of a lamp. To understand the theory of these processes, it is necessary to bear in mind the composition of the three following oxides of manganese:—

	Manganese.	Oxygen.	
Protoxide	27·7 or 1 equiv.	+ 8	=35·7
Sesquioxide	27·7	+ 12	=39·7
Peroxide	27·7	+ 16	=43·7

On applying a red heat to the last, it parts with half an equivalent of oxygen, and is converted into the sesquioxide. Every 43·7 grains of the peroxide will therefore lose, if quite pure, 4 grains of oxygen, or nearly 12 cubic inches; and one ounce will yield about 128 cubic inches of gas. With sulphuric acid the peroxide loses a whole eq. of oxygen, and is converted into the protoxide, which unites with the acid, forming a sulphate of the protoxide of manganese. Every 43·7 grains of peroxide yields 8 grains of oxygen and 35·7 of protoxide, which by uniting with one eq. (40) of the acid, forms 75·7 of the sulphate. The first of these processes is the most convenient in practice.

The gas obtained from peroxide of manganese, though hardly ever quite pure, owing to the presence of iron, carbonate of lime, and other earthy substances, is sufficiently good for ordinary purposes. It yields a gas of better quality, if previously freed from carbonate of lime by dilute hydrochloric or nitric acid; but when oxygen of great purity is required, it is better to obtain it from chlorate of potassa. For this purpose, the salt should be put into a retort of green glass, or of white glass made without lead, and be heated nearly to redness. It first becomes liquid, though quite free from water, and then, on increase of heat, is wholly resolved into pure oxygen gas, which escapes with effervescence, and into a white compound, called chloride of potassium, which is left in the retort. The composition of the chloric acid and potassa which constitute the salt, is stated below:—

Chlorine .	35·42 or 1 eq.	Potassium .	39·15 or 1 eq.
Oxygen .	40 or 5 eq.	Oxygen .	8 or 1 eq.
Chloric acid .	75·42 or 1 eq.	Potassa .	47·15 or 1 eq.

Hence the oxygen which passes over from the retort, is derived partly from the potassa and partly from the chloric acid ; while chlorine and potassium enter into combination. Thus are 122·57 grains of the chlorate resolved into 74·57 grains of chloride of potassium, and 48 grains, or about 161 cubic inches, of pure oxygen.

Properties.—Colourless, tasteless, inodorous ; feeble refraction of light ; non-conductor of electricity ; heavier than atmospheric air, sp. gr. being estimated at 1·1026 by Dulong and Berzelius, so that 100 cubic inches weigh at 60° and 30' Bar. 34·193 grains. It is always gaseous when not combined with other ponderable matter ; though even in its simplest form it is associated, like other elementary principles, with the agents productive of heat, light, and electricity. Like all gases it emits a strong heat when suddenly compressed : light also appears ; but this is solely due to its chemical action on the oil with which the compressing tube is lubricated. It is the most perfect — electric, always appearing at the + electrode when any of its compounds is electrolyzed ; is sparingly absorbed by water, which dissolves only 3 or 4 per cent. of the gas ; is neither acid nor alkaline, as it does not change the colour of blue flowers, nor evince a disposition to unite directly either with acids or alkalis. It has a very powerful attraction for most simple substances ; and there is not one of them with which it may not be made to combine. The act of combining with oxygen is called *oxidation*, and bodies which have united with it are said to be *oxidized*. The compounds so formed are divided by chemists into acids and oxides. The former division includes those compounds which possess the general properties of acids ; and the latter comprehends those which not only want that character, but of which many are highly alkaline, and yield salts by uniting with acids. The phenomena of oxidation are variable. It is sometimes produced with great rapidity, and with evolution of heat and light. Ordinary combustion, for instance, is nothing more than rapid oxidation ; and all inflammable or combustible substances derive their power of burning in the open air from their affinity for oxygen. On other occasions it takes place slowly, and without any appearance either of heat or light, as in the rusting of iron by moist air. Different as these processes may appear, oxidation is the result of both ; and both

depend on the same circumstance, namely, the presence of oxygen in the atmosphere.

All substances that are capable of burning in the open air, burn with far greater brilliancy in oxygen gas. A piece of wood, on which the least spark of light is visible, bursts into flame the moment it is put into a jar of oxygen; lighted charcoal emits beautiful scintillations; and phosphorus burns with so powerful and dazzling a light that the eye cannot bear its impression. Even iron and steel, which are not commonly ranked among the inflammables, undergo rapid combustion in oxygen gas.

The changes that accompany these phenomena are no less remarkable than the phenomena themselves. When a lighted taper is put into a vessel of oxygen gas, it burns for a while with increased splendour; but the size of the flame soon begins to diminish, and if the mouth of the jar be closed, the light will in a short time disappear entirely. The gas has now lost its characteristic property; for a second lighted taper, immersed in it, is instantly extinguished. This result is general. The burning of one body in a given portion of oxygen unfits it more or less completely for supporting the combustion of another; and the reason is manifest. Combustion is produced by the combination of inflammable matter with oxygen. The quantity of free oxygen, therefore, diminishes during the process, and is at length nearly or quite exhausted. The burning of all bodies, however inflammable, must then cease, because the presence of oxygen is necessary to its continuance. For this reason oxygen gas is called a supporter of combustion. Oxygen often loses its gaseous form as well as its other properties. If phosphorus or iron be burned in a jar of pure oxygen over water or mercury, the disappearance of the gas becomes obvious by the ascent of the liquid, which is forced up by the pressure of the atmosphere, and fills the vessel. Sometimes, on the contrary, the oxygen gas suffers diminution of volume only, or it may even undergo no change of bulk at all, as is exemplified by the combustion of the diamond.

The changes experienced by the burning body are equally striking. While the oxygen loses its power of supporting combustion, the inflammable substance lays aside its combustibility. It is then an oxidized body, and cannot be made to burn even by aid of the purest oxygen gas. It has also increased in weight. It is an error to suppose that bodies lose any thing while they burn. The ma-

terials of our fires and candles do indeed disappear, but they are not destroyed. Although they fly off in the gaseous form, and are commonly lost to us, it is not difficult to collect and preserve all the products of combustion. When this is done with the required care, the combustible matter is always found to weigh more after than before combustion; and the increase in weight is exactly equal to the quantity of oxygen which has disappeared during the process.

Oxygen gas is necessary to respiration. No animal can live in an atmosphere which does not contain a certain portion of uncombined oxygen; for an animal soon dies if put into a portion of air from which the oxygen has been previously removed by a burning body. Oxygen disappears during respiration. If a bird be confined in a limited quantity of atmospheric air, it will at first feel no inconvenience; but as a portion of oxygen is withdrawn at each inspiration, its quantity diminishes rapidly, so that respiration soon becomes laborious, and in a short time ceases altogether. Should another bird be then introduced into the same air, it will die in the course of a few seconds; or if a lighted candle be immersed in it, its flame will be extinguished. Respiration and combustion have therefore the same effect. An animal cannot live in an atmosphere which is unable to support combustion; nor, in general, can a candle burn in air which contains too little oxygen for respiration.

It is singular that, though oxygen is necessary to respiration, in a state of purity it is deleterious. When an animal, as a rabbit for example, breathes pure oxygen gas, no inconvenience is at first perceived; but after the interval of an hour or more the circulation and respiration become very rapid, and the system in general is highly excited. Symptoms of debility subsequently ensue, followed by insensibility; and death occurs in six, ten, or twelve hours. On examination after death, the blood is found highly florid in every part of the body, and the heart acts strongly even after the breathing has ceased. For these experiments we are indebted to Broughton. Its eq. is = 8; eq. vol. = 50; symb. O.

THEORY OF COMBUSTION.

The only phenomena of combustion noticed by an ordinary observer, are the destruction of the burning body, and the development of heat and light; but it has been demonstrated that in addition to these circumstances, oxygen gas invariably disappears, and a new compound consisting of oxygen and the combustible is gene-

rated. The term *combustion*, therefore, in its common signification, implies the rapid union of oxygen gas and combustible matter, accompanied with heat and light. As the evolution of heat and light is dependent on chemical action, the same phenomena may be expected in other chemical processes; and accordingly heat and light are frequently emitted quite independently of oxygen. Thus phosphorus takes fire, and a taper burns for a short time, in a vessel of chlorine; and several of the common metals, such as copper, antimony, and arsenic, in a state of fine division, become red hot when introduced into a jar of that gas. Potassium takes fire in cyanogen gas; and copper leaf or iron wire, if moderately heated, undergoes the same change in the vapour of sulphur. A mixture of iron filings and sulphur, when heated so as to bring the latter into perfect fusion, emits intense heat and light at the instant of combination; and a like effect, though in a far less degree, is produced by the action of concentrated sulphuric acid on pure magnesia. Most of these and similar examples, especially when one of the combining substances is gaseous, are frequently included under the idea of combustion; and they certainly belong to the same class of phenomena. In the subsequent observations, however, I shall employ the term in its ordinary sense; but the remarks concerning increase of temperature, whether with or without light, apply equally to all cases where heat is developed as a result of chemical action.

For many years prior to the discovery of oxygen gas, the phenomena of combustion were explained on the Stahlian or phlogistic hypothesis. All combustible bodies, according to Stahl, contain a certain principle which he called *phlogiston*, to the presence of which he ascribed their combustibility. He supposed that when a body burns, phlogiston escapes from it; and that when the body has lost phlogiston, it ceases to be combustible, and is then a dephlogisticated or incombustible substance. A metallic oxide was consequently regarded as a simple substance, and the metal itself as a compound of its oxide with phlogiston. The heat and light which accompany combustion were attributed to the rapidity with which phlogiston is evolved during the process.

The discovery of oxygen proved fatal to the Stahlian doctrine. Lavoisier had the honour of overthrowing it, and of substituting in its place the antiphlogistic theory. The basis of his doctrine has already been stated,—that combustion and oxidation in general

consist in the combination of combustible matter with oxygen. This fact he established beyond a doubt. On burning phosphorus in a jar of oxygen, he observed that a considerable quantity of the gas disappeared, that the phosphorus gained materially in weight, and that the increase of the latter exactly corresponded to the loss of the former. An iron wire was burnt in a similar manner, and the weight of the oxidized iron was found equal to that of the wire originally employed, added to the quantity of oxygen which had disappeared. That the oxygen is really present in the oxidized body he proved by a very decisive experiment. Some liquid mercury was confined in a vessel of oxygen gas, and exposed to a temperature sufficient for causing its oxidation. The oxide of mercury, so produced, was put into a small retort and heated to redness, when it was reconverted into oxygen and fluid mercury, the quantity of the oxygen being exactly equal to that which had combined with the mercury in the first part of the operation.

To account for the production of heat and light during combustion, Lavoisier had recourse to Black's Theory of latent heat. Heat is always evolved when a substance, without change of form, passes from a rarer into a denser state, and also when a gas becomes liquid or solid, or a liquid solidifies; because a quantity of heat previously combined, or latent, within it, is then set free. Now this is precisely what happens in many instances of combustion. Thus water is formed by the burning of hydrogen, in which case two gases give rise to a liquid; and in forming phosphoric acid with phosphorus, or in oxidizing metals, oxygen is condensed into a solid. When the product of combustion is gaseous, as in the burning of charcoal, the evolution of heat is ascribed to the circumstance that the oxidized body contains a smaller quantity of combined heat, or has a smaller sp. heat, than the substances by which it is produced.

This is the weak point of Lavoisier's theory. Chemical action is very often accompanied by increase of temperature, and the heat evolved during combustion is only a particular instance of it. Any theory, therefore, by which it is proposed to account for the production of heat in some cases, ought to be applicable to all. When combustion, or any other chemical action, is followed by considerable condensation, in consequence of which the new body contains less insensible heat than its elements did before combination, it is obvious that heat will, in that case, be disengaged. But if this were

the sole cause of the phenomenon, a rise of temperature should always be preceded by a corresponding diminution of sp. heat, and the extent of the former ought to be in a constant ratio with the degree of the latter. Now Petit and Dulong infer from their researches on this subject (*An. de Ch. et Ph.* x.), that the degree of heat developed during combination, bears no relation to the sp. heat of the combining substances; and that in the majority of cases, the evolution of heat is not attended by any diminution in the sp. heat of the compound. It is a well-known fact, that increase of temperature frequently attends chemical action, though the products contain much more insensible heat than the substances from which they were formed. This happens remarkably in the explosion of gunpowder, which is attended by intense heat; and yet its materials, in passing from the solid to the gaseous state, expand to at least 250 times their volume, and consequently render latent a large quantity of heat.

These circumstances leave no doubt that the evolution of heat during chemical action is owing to some cause quite unconnected with that assigned by Lavoisier; and if this cause operates so powerfully in some cases, it is fair to infer that part of the effect must be owing to it on those occasions, when the phenomena appear to depend on change of sp. heat alone. A new theory is therefore required to account for the chemical production of heat. But it is easier to perceive the fallacies of one doctrine, than to substitute another which shall be faultless; and it appears to me that chemists must, for the present, be satisfied with the simple statement, that energetic chemical action does of itself give rise to increase of temperature. Berzelius, in adopting the electro-chemical theory, regards the heat of combination as an electrical phenomenon, believing it to arise from the oppositely electrical substances neutralizing one another, in the same manner as the electric equilibrium is restored during the discharge of a Leyden jar. Electrical action certainly appears to be an essential part of every chemical change, and it is probable that the heat developed during the latter may be due to the former; but this part of science is as yet too imperfect for indicating the precise mode by which the effect is produced.

The heat emitted during combustion varies with the nature of the material. The effect of the combustible gases in raising the temperature of water, according to the experiments of Dalton, is shown in the following table.—(*Chemical Philosophy*, ii. 309.)

Hydrogen, in burning, raises an equal volume of water	5° F.
Carbonic oxide	4½
Light carburetted hydrogen	18
Olefiant gas	27
Coal gas, varies with the quality of the gas from	10 to 16
Oil gas, varies also with the quality of the gas from	12 to 20

Dalton further states that generally the combustible gases give out heat nearly in proportion to the oxygen which they consume.

Despretz has given a notice of some experiments on the heat developed in combustion (An. de Ch. et Ph. xxxvii. 180). The substances burned were hydrogen, carbon, phosphorus, and several metals; and so much of each was employed, as to require the same quantity of oxygen. When the combustion of hydrogen gas produced 2578 degrees of heat, carbon gave out 2967, and iron 5325. Phosphorus, zinc, and tin, emit quantities of heat very nearly the same as iron. Hence it follows that, for equal quantities of oxygen, hydrogen in burning evolves less heat than most other substances. These results do not accord with those of Dalton.

SECTION IV.

HYDROGEN.

Hist.—FIRST correctly described in 1766 by Cavendish (Phil. Trans. lvi. 144), under the name of *inflammable air*. It had been previously confounded with other combustible gases, and it was by some called *phlogiston*, from the notion that it is the matter of heat. Its present name is derived from *ὕδωρ* water, and *γεννέειν* to generate.

Prep.—Commonly in two ways. The first consists in passing the vapour of water over metallic iron heated to redness. This is done by putting iron wire into a gun-barrel open at both ends, to one of which is attached a retort containing pure water, and to the other a bent tube. The gun-barrel is placed in a furnace, and when it has acquired a full red heat, the water in the retort is made to boil briskly. The gas, which is copiously disengaged as soon as the steam comes in contact with the glowing iron, passes along the bent tube, and may be collected in convenient vessels, by dipping the free extremity of the tube into the water of a pneumatic trough. The second and more convenient method consists in putting pieces of iron or zinc into dilute sulphuric acid, formed of one part of strong acid and four or five of water. Zinc

is generally preferred. The hydrogen obtained in these processes is not absolutely pure. The gas evolved during the solution of iron has an offensive odour, ascribed by Berzelius to the presence of a volatile oil, which may be almost entirely removed by transmitting the gas through alcohol. The oil appears to arise from some compound being formed between hydrogen and the carbon which is always contained even in the purest kinds of common iron; and it is probable that a little carburetted hydrogen gas is generated at the same time. The zinc of commerce contains sulphur, and almost always traces of charcoal, in consequence of which it is contaminated with hydro-sulphuric acid, and probably with the same impurities, though in a less degree, as are derived from iron. A little metallic zinc is also contained in it, apparently in combination with hydrogen. All these impurities, carburetted hydrogen excepted, may be removed by passing the hydrogen through a solution of pure potassa. To obtain hydrogen of great purity, distilled zinc should be employed.

Prop.—Colourless, inodorous, tasteless; always gaseous when uncombined; a powerful refractor of light; the lightest body in nature, and hence the best material for filling balloons. From its extreme lightness it is difficult to ascertain its sp. gr. by weighing, because the presence of minute quantities of common air or watery vapour occasions considerable error. By the table of sp. gravities (page 231) it appears that hydrogen gas is just 16 times lighter than oxygen, an inference derived from the composition of water to be shortly stated: hence 100 C. I. 60° and 30 Bar. should weigh $\frac{1}{16} \times 34.193 = 2.1371$ grains, and its sp. gr. should be 0.06896.

It is neither acid nor alkaline. Water dissolves only $1\frac{1}{2}$ per cent. of its volume. It cannot support respiration: death ensues from deprivation of oxygen rather than from any noxious quality of the hydrogen, since an atmosphere composed of a due proportion of oxygen and hydrogen gases may be respired without inconvenience. Nor is it a supporter of combustion; for when a lighted candle fixed on wire is passed up into an inverted jar full of hydrogen gas, the light instantly disappears.

Hydrogen gas is inflammable in an eminent degree, though, like other combustibles, it requires the aid of a supporter of combustion, burning only where it is in contact with the air. Its combustion, when conducted in this manner, goes on tranquilly, and is attended with a yellowish blue flame and a very feeble light. The phenomena

are different when the hydrogen is previously mixed with a due quantity of air. The approach of flame not only sets fire to the gas near it, but the whole is kindled at the same instant; and a flash of light passes through the mixture, followed by a violent explosion. The best proportion for the experiment is two measures of hydrogen to five or six of air. The explosion is far more violent when pure oxygen is used instead of atmospheric air, particularly when the gases are mixed together in the ratio of one measure of oxygen to two of hydrogen.

Oxygen and hydrogen gases cannot combine at ordinary temperatures, and may, therefore, be kept in a state of mixture without even gradual combination taking place between them. Hydrogen may be set on fire, when in contact with air or oxygen gas, by flame, by a solid body heated to bright redness, and by the electric spark. If a jet of hydrogen gas be thrown upon recently prepared spongy platinum, this metal almost instantly becomes red hot, and then sets fire to the gas, a discovery which was made in the year 1824 by Professor Doebereiner of Jena. The power of flame and electricity in causing a mixture of hydrogen with air or oxygen gas to explode, is limited. Mr. Cavendish found that flame occasions a very feeble explosion when the hydrogen is mixed with nine times its bulk of air; and that a mixture of four measures of hydrogen with one of air does not explode at all. An explosive mixture formed of two measures of hydrogen and one of oxygen gas, explodes from all the causes above enumerated. Biot found that sudden and violent compression likewise causes an explosion, apparently from the heat emitted during the operation; for an equal degree of condensation, slowly produced, has not the same effect. The electric spark ceases to cause detonation when the explosive mixture is diluted with twelve times its volume of air, fourteen of oxygen, or nine of hydrogen; or when it is expanded to sixteen times its bulk by diminished pressure. Spongy platinum acts just as rapidly as flame or the electric spark in producing explosion, provided the gases are quite pure and mixed in the exact ratio of two to one.* Mr. Faraday finds that platinum foil, if perfectly clean, produces

* For a variety of facts respecting the causes which prevent the action of flame, electricity, and platinum in producing detonation, the reader may consult the Essay of M. Grotthus in the *Ann. de Chimie*, vol. lxxii.; Sir H. Davy's work on Flame; Dr. Henry's Essay in the *Philosophical Transactions* for 1824; and a paper by myself in the *Edinburgh Philosophical Journal* for the same year.

gradual though rather rapid combination of the gases, often followed by explosion. (Phil. Trans. 1834.)

When the action of heat, the electric spark, and spongy platinum no longer cause explosion, a silent and gradual combination between the gases may still be occasioned by them. Sir H. Davy observed that oxygen and hydrogen gases unite slowly with one another, when they are exposed to a temperature above the boiling point of mercury, and below that at which glass begins to appear luminous in the dark. An explosive mixture diluted with air to too great a degree to explode by electricity, is made to unite silently by a succession of electric sparks. Spongy platinum causes them to unite slowly, though mixed with one hundred times their bulk of oxygen gas.

A large quantity of heat is evolved during the combustion of hydrogen gas. Lavoisier concludes from experiments made with his calorimeter, (Elements, vol. i.) that one pound of hydrogen occasions as much heat in burning as is sufficient to melt 295.6 pounds of ice. Dr. Dalton fixes the quantity of ice at 320 pounds, and Dr. Crawford at 480. The most intense heat that can be produced, is caused by the combustion of hydrogen in oxygen gas. Dr. Hare of Philadelphia, who first burned hydrogen for this purpose, collected the gases in separate gas-holders, from which a stream was made to issue through tubes communicating with each other, just before their termination. At this point the jet of the mixed gases was inflamed. The effect of the combustion, though very great, is materially increased by forcing the two gases in due proportion into a strong metallic vessel by means of a condensing syringe, and setting fire to a jet of the mixture as it issues. An apparatus of this kind, now known by the name of the oxy-hydrogen blowpipe, was contrived by Mr. Newman, and employed by the late Professor Clarke in his experiments on the fusion of refractory substances. On opening a stop-cock which confines the compressed gases, a jet of the explosive mixture issues with force through a small blowpipe tube, at the extremity of which it is kindled. In this state, however, the apparatus should never be used; for as the reservoir is itself full of an explosive mixture, there is great danger of the flame running back along the tube, and setting fire to the whole gas at once. To prevent the occurrence of such an accident, which would most probably prove fatal to the operator, Professor Cumming proposed that the gas, as it issues from the reservoir, should be made

to pass through a cylinder full of oil or water before reaching the point at which it is to burn; and Dr. Wollaston suggested the additional precaution of fixing successive layers of fine wire gauze within the exit tube, each of which would be capable of intercepting the communication of flame. A modification of this apparatus has been devised by Mr. Gurney; but both his and Newman's are rendered unnecessary by the safety tube lately proposed by Mr. Hemming. It consists of a brass cylinder, about 6 inches long, and $\frac{3}{4}$ ths of an inch wide, filled with very fine brass wire in length equal to that of the tube. A pointed rod of metal, $\frac{1}{8}$ th of an inch thick, is then forcibly inserted through the centre of the bundle of wires in the tube, so as to wedge them tightly together. The interstices between the wires thus constitute very fine metallic tubes, the conducting power of which is so great as entirely to intercept the passage of flame. The mixed gases are supplied from a common bladder. (Phil. Mag. 3rd S. i. 82.) A very intense heat may be safely and easily procured by passing a jet of oxygen gas through the flame of a spirit lamp, as proposed by the late Dr. Marcet. An elegant improvement on this principle has been devised by Mr. Daniell, by fixing a jet for conveying oxygen within another jet for hydrogen or coal gas, so that a current of oxygen may be introduced into the middle of the flame. (Phil. Mag. ii. 57. 3rd Series.) The heat from this apparatus is quite sufficient for most purposes; and it may be still further increased by causing the gases to pass separately through heated tubes, in order that they may have a temperature of 400° or 500° on issuing from the jets.—On this principle is founded the patent of Mr. Dunlop, of the Carron Iron Works, for increasing the temperature of blast furnaces: the air which supports the combustion is previously heated by transmission through iron tubes kept at a low red heat, whereby the power of the furnaces is surprisingly increased, and a great saving in fuel and time is accomplished.

Its eq. is = 1; eq. vol. = 100; Symb. H. Compounds with oxygen:—

	By Weight.			By Volume.	
	Hydrogen.	Oxygen.	Equiv.	Hyd.	Oxy.
Water (Protoxide of Hydrogen)	1 or 1 eq.	+ 8 or 1 eq.	= 9	100	50
Peroxide of Hydrogen	1 or 1 eq.	+ 16 or 2 eq.	= 17	100	100

Water.—First proved by Cavendish to be the sole product of the combustion of hydrogen gas. He demonstrated it by burning oxy-

gen and hydrogen gases in a dry glass vessel, when a quantity of pure water was generated, exactly equal in weight to that of the gases which had disappeared. This experiment, which is the synthetic proof of the composition of water, was afterwards made on a much larger scale in Paris by Vauquelin, Fourcroy, and Seguin. Lavoisier first demonstrated its nature analytically, by passing a known quantity of watery vapour over metallic iron heated to redness in a glass tube. Hydrogen gas was disengaged, the metal in the tube was oxidized, and the weight of the former, added to the increase which the iron had experienced from combining with oxygen, exactly corresponded to the quantity of water decomposed.

Its composition by volume was demonstrated very satisfactorily by Nicholson and Carlisle: by resolving water into its elements by galvanism, and collecting them in separate vessels, they obtained precisely two measures of hydrogen and one of oxygen,—a result which has been fully confirmed by subsequent experimenters. The same fact was proved synthetically by Gay-Lussac and Humboldt, in their Essay on Eudiometry, published in the *Journal de Physique* for 1805. They found that when a mixture of oxygen and hydrogen is inflamed by the electric spark, those gases always unite in the exact ratio of one to two, whatever may be their relative quantity in the mixture. When one measure of oxygen is mixed with three of hydrogen, one measure of hydrogen remains after the explosion; and a mixture of two measures of oxygen and two of hydrogen leaves one measure of oxygen. When one volume of oxygen is mixed with two of hydrogen, both gases, if quite pure, disappear entirely on the electric spark being passed through them. The composition of water by weight was determined with great care by Berzelius and Dulong; and we cannot hesitate, considering the known dexterity of the operators, and the principle on which their method of analysis was founded, to regard their result as a nearer approximation to the truth than that of any of their predecessors. They state, as a mean of three careful experiments (*Ann. de Ch. et Ph.* xv.) that 100 parts of pure water consist of 11.1 of hydrogen and 88.9 oxygen, which is the ratio of 1 to 8.009, very nearly that of 1 to 8 above stated.

The processes for procuring a supply of hydrogen gas will now be intelligible. The first is the method by which Lavoisier made the analysis of water. It is founded on the fact that iron at a red heat decomposes water, the oxygen of that liquid uniting with the metal, and the hydrogen gas being set free. That the hydrogen which is

evolved when zinc or iron is put into dilute sulphuric acid must be derived from the same source, is obvious from the consideration, that of the three substances, iron, sulphuric acid, and water, the last is the only one which contains hydrogen. The product of the operation, besides hydrogen, is sulphate of the protoxide of iron, if iron is used, or of the oxide of zinc, when zinc is employed. The knowledge of the combining proportions of these substances will readily give the exact quantity of each product. These numbers are—

Water (8 oxy. + 1 hyd.)	9
Sulphuric acid	40.1
Iron	28
Protoxide of iron (28 iron + 8 oxygen)	36
Sulphate of the protoxide of iron (40.1 + 36)	76.1

Hence for every 9 grains of water which are decomposed, 1 grain of hydrogen will be set free; 8 grains of oxygen will unite with 28 grains of iron, forming 36 of the protoxide of iron; and the 36 grains of protoxide will combine with 40.1 grains of sulphuric acid, yielding 76.1 of sulphate of the protoxide of iron. A similar calculation may be employed when zinc is used, merely by substituting the equivalent of zinc (32.5) for that of iron.—According to Mr. Cavendish, an ounce of zinc yields 676 cubic inches, and an equal quantity of iron 782 cubic inches of hydrogen gas.

The action of dilute sulphuric acid on metallic zinc affords an instance of what was once called *Disposing Affinity*. Zinc decomposes pure water at common temperatures with extreme slowness; but as soon as sulphuric acid is added, decomposition of the water takes place rapidly, though the acid merely unites with oxide of zinc. The former explanation was, that the affinity of the acid for oxide of zinc disposed the metal to unite with oxygen, and thus enabled it to decompose water; that is, the oxide of zinc was supposed to produce an effect previous to its existence. The obscurity of this explanation arises from regarding changes as consecutive, which are in reality simultaneous. There is no succession in the process; the oxide of zinc is not formed previously to its combination with the acid, but at the same instant. There is, as it were, but one chemical change, which consists in the combination at one and the same moment of zinc with oxygen, and of oxide of zinc with the acid; and this change occurs because these two affinities, acting together, overcome the attraction of oxygen and hydrogen for one another.

Prop.—Transparent, colourless, inodorous, tasteless ; powerful refractor of light ; imperfect conductor of heat and electricity ; very incompressible, its absolute diminution for a pressure of one atmosphere being only 51·3 millionths of its volume. (An. de Ch. et Ph. xxxvi. 140.) Its changes of form under varying temperatures have been already stated in the section on heat. Its sp. gr. is 1, being the unit to which the sp. gr. of all solids and liquids is referred as a convenient term of comparison (page 119). One cubic inch, at 62° and 30 Bar., weighs 252·458 grains, both being at 62° and 30 Bar., or 769·4 at 32° and 30 Bar. It is 815 times heavier than atmospheric air. The sp. gr. of aqueous vapour is 0·6202, and 100 C. I. (containing 100 hydrogen and 50 oxygen), at 212° and 30 Bar., weigh 14·96 grains ; sp. gr. of ice is 0·92.

Owing partly to the extensive range of its own affinity, and partly to the nature of its elements, water is a chemical agent of great power. Of this, the preparation of hydrogen gas is an example ; and indeed there are few complex changes, where oxygen and hydrogen are present, which do not give rise either to the production or decomposition of water. But, independently of the elements of which it is composed, it combines directly with many bodies. Sometimes it is contained in a variable ratio, as in ordinary solution ; in other compounds it is present in a fixed definite proportion, as is exemplified by its union with several of the acids, the alkalies, and all salts that contain water of crystallization. These combinations are termed *hydrates*. Thus, concentrated sulphuric acid is a compound of one eq. of the real acid and one eq. of water ; and its proper name is *hydrous sulphuric acid*, or *hydrate of sulphuric acid*. The prefix *hydro* has been sometimes used to signify the presence of water in definite proportion ; but it is advisable, to prevent mistakes, to limit its employment to the compounds of hydrogen.

The purest water which can be found as a natural product, is procured by melting freshly fallen snow, or by receiving rain in clean vessels at a distance from houses. But this water is not absolutely pure ; for if placed under the exhausted receiver of an air pump, or boiled briskly for a few minutes, bubbles of gas escape from it. The air obtained in this way from snow water is much richer than atmospheric air in oxygen gas. According to Gay-Lussac and Humboldt, it contains 34·8 per cent of oxygen, and the air separated by ebullition from rain water contains 32 per cent. All water which has

once fallen on the ground becomes impregnated with more or less earthy or saline matters, and can be separated from them only by distillation. The distilled water, thus obtained, and preserved in clean well-stopped bottles, is absolutely pure. Recently boiled water has the property of absorbing a portion of all gases, when its surface is in contact with them; and the absorption is promoted by brisk agitation. The following table, from Henry's Chemistry, shows the absorbability of different gases by water, deprived of all its air by ebullition.

100 C. I. water, at 60° and 30 Bar., absorb of

	Dalton and Henry.	Saussure.
Sulphuretted hydrogen	100 C. I.	253
Carbonic acid	100	106
Nitrous oxide	100	76
Oleasant gas	12.5	15.3
Oxygen	3.7	6.5
Carbonic oxide	1.56	6.2
Nitrogen	1.56	4.1
Hydrogen	1.56	4.6

The estimate of Saussure is in general too high. That of Dalton and Henry for nitrous oxide, according to the experiments of Davy, is considerably beyond the truth.

Its eq. is = 9; eq. vol. 100; symb. $H + O$, or HO , or H , or aq. from aqua.

Peroxide or Binoxide.—Discovered by Thenard in 1818. Its preparation is founded on the fact that there are two oxides of barium, the peroxide and protoxide; the former of which is converted into the protoxide by the action of acids. When this process is conducted with the necessary precautions, the oxygen which is set free, instead of escaping in the form of gas, unites with the hydrogen of the water, and brings it to a maximum of oxidation. For a full detail of all the minutiae of the process, the reader may consult the original memoir of Thenard;* the general directions are the following:—To six or seven ounces of water add so much pure concentrated hydrochloric acid as is sufficient to dissolve 230 grains of baryta; and after having placed the mixed fluids in a glass vessel surrounded with ice, add in successive portions 185 grains of peroxide of barium reduced to powder, and stir with a glass rod after each addition. When the solution, which takes place without effer-

* In the *An. de Chim. et de Phys.* vol. viii. ix. x. and l.; *Annals of Philosophy*, vol. xiii. and xiv.; and M. Thenard's *Traité de Chimie*.

vescence, is complete, sulphuric acid is added in sufficient quantity for precipitating the whole of the baryta in the form of an insoluble sulphate, leaving the hydrochloric acid in solution. Another portion of peroxide of barium, amounting to 185 grains, is then put into the liquid: the free hydrochloric acid instantly acts upon it, and as soon as it is dissolved, the baryta is again separated as a sulphate by the addition of sulphuric acid. The solution is then filtered, in order to separate the insoluble sulphate of baryta; and fresh quantities of peroxide of barium are added in succession, till about three ounces have been employed. The liquid then contains from 25 to 30 times its volume of oxygen gas. The hydrochloric acid which has served to decompose the peroxide of barium during the whole process, is now removed by the cautious addition of sulphate of oxide of silver, and the sulphuric acid afterwards separated by solid baryta.

Peroxide of hydrogen, as thus prepared, is still diluted with a considerable quantity of water. To separate the latter, the mixed liquids are placed, with a vessel of strong sulphuric acid, under the exhausted receiver of an air pump. As the water evaporates, the density of the residue increases, till at last it acquires the sp. gr. of 1.452. The concentration cannot be pushed further; for if kept under the receiver after reaching this point, the peroxide itself gradually but slowly volatilizes without change.

Prop.—A colourless transparent liquid, inodorous, and of a metallic taste; volatilizes *in vacuo* less rapidly than water; retains its liquid form at all degrees of cold to which it has been exposed; at 59° is resolved into oxygen and water, and hence should be always kept in glass tubes surrounded by ice. It intermixes with water in all proportions; bleaches litmus and turmeric paper, whitens the skin and tongue, causing to both a pricking sensation, and thickens the saliva. The most remarkable of its properties is its facility of decomposition. Diffused daylight does not seem to exert any influence over it, and even the direct solar rays act upon it tardily. It effervesces from escape of oxygen at 59°, and the sudden application of a higher temperature, as that of 212°, gives rise to such rapid evolution of gas as to cause an explosion. Water, apparently by combining with the peroxide, renders it more permanent; but no degree of dilution can enable it to bear the heat of boiling water, at which temperature it is entirely decomposed. All the metals except iron, tin, antimony, and tellurium, have a tendency

to decompose it, converting it into oxygen and water. A state of minute mechanical division is essential for producing rapid decomposition. If the metal is in mass, and the peroxide diluted with water, the action is slow. The metals which have a strong affinity for oxygen are oxidized at the same time, such as potassium, sodium, arsenic, molybdenum, manganese, zinc, tungsten, and chromium; while others, such as gold, silver, platinum, iridium, osmium, rhodium, palladium, and mercury, retain the metallic state.

It is decomposed at common temperatures by many of the metallic oxides. That some protoxides should have this effect, would be anticipated in consequence of their tendency to pass into a higher state of oxidation. The protoxides of iron, manganese, tin, cobalt, and others, act on this principle, and are really converted into peroxides. The peroxides of barium, strontium, and calcium may likewise be formed by the action of peroxide of hydrogen on baryta, strontia, and lime. But it is a singular fact, of which no satisfactory explanation has been given, that some oxides decompose it without passing into a higher degree of oxidation. The peroxides of lead, mercury, gold, platinum, manganese, and cobalt, possess this property in the greatest perfection, acting on peroxide of hydrogen, when concentrated, with surprising energy. The decomposition is complete and instantaneous; oxygen gas is evolved so rapidly as to produce a kind of explosion; and such intense temperature is excited, that the glass tube in which the experiment is conducted becomes red-hot. The reaction is very great even when the peroxide of hydrogen is diluted with water. Oxide of silver occasions very perceptible effervescence when put into water which contains only 1-50th of its bulk of oxygen. All the metallic oxides, which are decomposed by a red heat, such as those of gold, platinum, silver, and mercury, are reduced to the metallic state when they act upon peroxide of hydrogen. This effect cannot be altogether ascribed to heat disengaged during the action; for oxide of silver suffers reduction when put into a very dilute solution of the peroxide, although the decomposition is not then attended by an appreciable rise of temperature.

While the tendency of metals and metallic oxides is to decompose the peroxide of hydrogen, acids have the property of rendering it more stable. In proof of this, let a portion of that liquid, somewhat diluted with water, be heated till it begins to effervesce from the escape of oxygen gas; let some strong acid, as the nitric, sul-

phuric, or hydrochloric, be then dropped into it, and the effervescence will cease on the instant. When a little finely divided gold is put into a weak solution of peroxide of hydrogen, containing only 10, 20, or 30 times its bulk of oxygen, brisk effervescence ensues; but on letting one drop of sulphuric acid fall into it, effervescence ceases instantly; it is reproduced by the addition of potassa, and is again arrested by adding a second portion of acid. The only acids that do not possess this property are those that have a low degree of acidity, as carbonic and boracic acids; or those which suffer a chemical change when mixed with peroxide of hydrogen, such as hydriodic, hydrosulphuric, and sulphurous acids. Acids appear to increase the stability of the peroxide in the same way as water does, namely, by combining chemically with it. Several compounds of this kind were formed by Thenard, before he was aware of the existence of the peroxide of hydrogen. They were made by dissolving peroxide of barium in some dilute acid, such as the nitric, and then precipitating the baryta by sulphuric acid. As nitric acid was supposed under these circumstances to combine with an additional quantity of oxygen, Thenard applied the term oxygenized nitric acid to the resulting compound, and described several other new acids under a similar title. But the subsequent discovery of peroxide of hydrogen put the nature of the oxygenized acids in a clearer light; for their properties are easily explicable on the supposition that they are composed, not of acids and oxygen gas, but of acids united with peroxide of hydrogen.

Peroxide of hydrogen was analysed by diluting a known weight of it with water, and then decomposing it by boiling the solution.

Its eq. is = 17; symb. $H + 2O$, or HO_2 , or \ddot{H} .

SECTION V.

NITROGEN.

Hist.—FIRST noticed by Rutherford of Edinburgh in 1772. Discovered to be a constituent of the atmosphere by Lavoisier in 1775, and by Scheele about the same time. It was termed azote (α privative, and $\zeta\omega\eta$, *life*;) by Lavoisier, from its inability to support respiration. The name of nitrogen is derived from its being an element of nitric acid.

Prep.—1. By burning a piece of phosphorus in a jar full of air

inverted over water. The strong affinity of phosphorus for oxygen enables it to burn till the whole of that gas is consumed. The product of the combustion, metaphosphoric acid, is at first diffused through the residue in the form of a white cloud; but as this substance is rapidly absorbed by water, it disappears entirely in the course of half an hour. The residual gas is nitrogen, containing a small quantity of carbonic acid and vapour of phosphorus, both of which may be removed by agitating it briskly with a solution of pure potassa. Several other substances may be employed for withdrawing oxygen from atmospheric air. A solution of protosulphate of iron, charged with binoxide of nitrogen, absorbs the oxygen in the space of a few minutes. A stick of phosphorus produces the same effect in twenty-four hours, if exposed to a temperature of 60°. A solution of sulphuret of potassium or calcium acts in a similar manner; and a mixture of equal parts of iron filings and sulphur, made into a paste with water, may be employed with the same intention. Both these processes, however, are inconvenient from their slowness.—2. By exposing a mixture of fresh muscle and nitric acid of sp. gr. 1.20 to a moderate temperature. Effervescence then takes place, and a large quantity of gaseous matter is evolved, which is nitrogen mixed with a little carbonic acid. The latter must be removed by agitation with lime water; but the residue still retains a peculiar odour, indicative of the presence of some volatile principle which cannot be wholly separated from it. The theory of this process is somewhat complex, and will be considered more conveniently in a subsequent part of the work. 3. By transmitting chlorine gas through a solution of ammonia, when that alkali yields its hydrogen to the chlorine, and its nitrogen is evolved.

Prop.—Colourless, tasteless, inodorous; always gaseous when uncombined; sp. gr. 0.9722, so that 100 C.I. weigh 30.166 grains; no action on the blue colour of plants; water dissolves $1\frac{1}{2}$ per cent. It is distinguished from other gases more by negative characters than by any striking quality. It is not a supporter of combustion; but, on the contrary, extinguishes all burning bodies that are immersed in it. No animal can live in it; but yet it exerts no injurious action either on the lungs or on the system at large, the privation of oxygen gas being the sole cause of death. It is not inflammable like hydrogen; though, under favourable circumstances, it may be made to unite with oxygen.

Considerable doubt exists as to the nature of nitrogen. Though

ranked among the simple non-metallic bodies, some circumstances have led to the suspicion that it is compound; and this opinion has been warmly advocated by Davy and Berzelius. The chief argument in favour of this view is drawn from the phenomena that attend the formation of what is called the *ammoniacal amalgam*. From the metallic appearance of this substance, it was supposed to be a compound of mercury and a metal; and as the only method of forming it is by the action of galvanism on a salt of ammonia, in contact with a globule of mercury, it follows that the metal, if present at all, must have been supplied by the ammonia. Now ammonia is composed of hydrogen and nitrogen; and as the former, from its small sp. gravity, can hardly be supposed to contain a metal, it was inferred that it must be present in the latter. Unfortunately for this argument, the supposed metal cannot be obtained in a separate state. The amalgam no sooner ceases to be under galvanic influence than its elements begin to separate spontaneously, and in a few minutes decomposition is complete, the sole products being ammonia, hydrogen, and pure mercury. Davy accounted for this change on the supposition that water is decomposed; that its oxygen reproduces nitrogen by uniting with the supposed metal; and that one part of its hydrogen forms ammonia by uniting with the nitrogen, while the remainder escapes in the form of gas. But Gay-Lussac and Thenard (*Recherches Physico-Chimiques*, vol. i.) declare that the amalgam resolves itself into mercury, ammonia, and hydrogen, even though perfectly free from moisture; and they infer from their experiments that it is composed of those three substances combined directly with each other. It hence appears that the examination of the ammoniacal amalgam affords no proof of the compound nature of nitrogen; nor was Davy's attempt to decompose that gas by aid of potassium, intensely heated by a galvanic current, attended with better success.

Its eq. is 14.15; eq. vol. = 100; symb. N.

The compounds of nitrogen treated of in this section are the following, exclusive of atmospheric air, which is regarded as a mechanical mixture:—

	By volume.		By weight.		Formulae.
	Nit.	Oxy.	Nit.	Oxy. Equiv.	
Nitrous oxide	100	. 50	14.15+8	= 22.15	N+O
Nitric oxide	100	. 100	14.15+16	= 30.15	N+2O

	By volume.		By weight.		Equiv.	Formulae.
	Nit.	Oxy.	Nit.	Oxy.		
Hyponitrous acid	100	. 150	14.15+24 =	38.15	N+3O	
Nitrous acid	100	. 200	14.15+32 =	46.15	N+4O	
Nitric acid	100	. 250	14.15+40 =	44.15	N+5O	

ON THE ATMOSPHERE.

The earth is everywhere surrounded by a mass of gaseous matter called the atmosphere, which is preserved at its surface by the force of gravity, and revolves together with it around the sun. It is colourless and invisible, excites neither taste nor smell when pure, and is not sensible to the touch unless when it is in motion. It possesses the physical properties of elastic fluids in a high degree. Its sp. gr. is unity, being the standard with which the density of all gaseous substances is compared. At 30 Bar. and 32° it is 769.4 times lighter than water, and 10462 than mercury; or at 62°, 815 times lighter than water, and nearly 11065 times lighter than mercury. The knowledge of its exact weight is an essential element in many physical and chemical researches, and has been determined with very great care by Prout, who finds that 100 C. I. of pure and dry atmospheric air, at 60° and 30 Bar. weigh 31.0117 grains.

The pressure of the atmosphere was first noticed early in the 17th century by Galileo, and was afterwards demonstrated by his pupil Torricelli, to whom science is indebted for the invention of the barometer. Its pressure at the level of the sea is equal to a weight of about 15 pounds on every square inch of surface, and is capable of supporting a column of water 34 feet high, and one of mercury of 30 inches; that is, a column of mercury of one inch square and 30 inches long has the same weight (nearly 15 pounds) as a column of water of equal base and 34 feet long, and as a column of air of equal base reaching from the level of the sea to the extreme limit of the atmosphere. By the use of the barometer it was discovered that the atmospheric pressure is variable. It varies according to the elevation above the level of the sea, and on this principle the height of mountains is estimated. Supposing the density of the atmosphere to be uniform, a fall of one inch in the barometer would correspond to 11065 inches, or 922 feet of air; but in order to make the calculation with accuracy, allowance must be made for the increasing rarity of the air, and for various other circumstances

which are detailed in works on meteorology. (Daniel's *Meteorological Essays*, 2nd edit. 376.) From causes at present not understood, the pressure varies likewise at the same place. On this depends the indications of the barometer as a weather-glass; for observation has fully proved, that the weather is commonly fair and calm when the barometer is high, and usually wet and stormy when the mercury falls.

Atmospheric air is highly compressible and elastic, so that its particles admit of being approximated to a great extent by compression, and expand to an extreme degree of rarity, when the tendency of its particles to separate is not restrained by external force. The volume of air and all other gaseous fluids, so long as they retain the elastic state, is inversely as the pressure to which they are exposed. Thus a portion of air which occupies 100 measures when compressed by a force of one pound, will be diminished to 50 measures when the pressure is doubled, and will expand to 200 measures when the compression is equal to half a pound. This law was first demonstrated in 1662 by the celebrated Boyle, and a second demonstration of it was given some years afterwards by the French philosopher Mariotte, apparently without being aware that the discovery had been previously made in England. It is hence frequently called the law of Meriotte. Till lately it had not been verified for very great pressures; but from the experiments of Oersted in 1825, who extended his observations to air compressed by a force equal to 110 atmospheres, it may be inferred to be quite general, except when the gaseous matter assumes the liquid form. (Ed. *Journal of Science*, iv. 224.) Gases vary from this law when they approach the point at which they assume the liquid form. At what pressure air becomes liquid is uncertain, since all attempts to condense it have hitherto been unsuccessful.

The extreme compressibility and elasticity of the air accounts for the facility with which it is set in motion, and the velocity with which it is capable of moving. It is subject to the laws which characterize elastic fluids in general. It presses, therefore, equally on every side; and when some parts of it become lighter than the surrounding portions, the denser particles rush rapidly into their place and force the more rarified ones to ascend. The motion of air gives rise to various familiar phenomena. A stream or current of air is wind, and an undulating vibration excites the sensation of sound.

The atmosphere is not of equal density at all its parts. This is obvious from the consideration, that those portions which are next the earth sustain the whole pressure of the atmosphere, while the higher strata bear only a part. The atmospheric column diminishes in length as the distance from the earth's surface increases; and, consequently, the greater the elevation, the lighter must be the air. It is not known to what height the atmosphere extends. From calculations founded on the phenomena of refraction, its height is supposed to be about 45 miles; and Wollaston estimated, from the law of expansion of gases, that it must extend to at least 40 miles with properties unimpaired by rarefaction. In speculating on its extent beyond that distance, it becomes a question whether the atmosphere is or is not limited to the earth. This subject was discussed with his usual sagacity by Wollaston in an *Essay on the Finite Extent of the Atmosphere* (Phil. Trans. 1822). Supposing the atmosphere unlimited, it should pervade all space, and accumulate about the sun, moon, and planets, forming around each an atmosphere, the density of which would depend on their respective forces of attraction. Now Wollaston inferred from astronomical observations made by himself and Kater, that there is no solar atmosphere; and the observations of other astronomers appear to justify the same inference with respect to the planet Jupiter. If the accuracy of these conclusions be admitted, it follows that our atmosphere is confined to the earth; and it may next be asked, by what means is its extent limited? Wollaston accounted for it by supposing the air, after attaining a certain degree of rarefaction, to possess such feeble elasticity, that the tendency of its particles to separate further from each other is counteracted by gravity. The unknown height at which this equilibrium between the two forces of elasticity and gravitation takes place, is the extreme limit of the atmosphere. The loss of elasticity may be ascribed to two powerful and concurring causes; namely, to the distance between the particles of air when highly rarefied, and to the extreme cold which prevails in the higher strata of the atmosphere.

The temperature of the atmosphere varies with its elevation. Gaseous fluids permit radiant matter to pass freely through them without any absorption, and therefore without their temperature being influenced by its passage. The atmosphere is not heated by transmitting the rays of the sun, but receives its heat solely from

the earth, and chiefly by actual contact ; so that its temperature becomes progressively lower, as the distance from the general mass of the earth increases. Another circumstance which contributes to the same effect, is the increasing tenuity of the atmosphere ; for the temperature of rarefied air is less raised by a given quantity of heat, than that of the same portion of air when compressed, owing to its sp. heat being greater in the former state than in the latter. From the joint influence of both these causes it is found that, in ascending into the atmosphere, the temperature diminishes at the rate of one degree for about every 352 feet. The rate of decrease is probably much slower at considerable distances from the earth ; but still there is no reason to doubt that the temperature continues to decrease with the increasing elevation. There must consequently in every latitude be a point, where the thermometer never rises above 32°, and where ice is never liquefied. This point varies with the latitude, being highest within the tropics and descending gradually as we advance towards the poles. The following table, from the Supplement to the Encyclopedia Britannica, page 190, article Climate, shows the point of perpetual ice corresponding to different latitudes.

Latitude.	English feet in height	Latitude.	English feet in height.
0° . .	15,207	45° . .	7,671
5° . .	15,095	50° . .	6,334
10° . .	14,764	55° . .	5,034
15° . .	14,220	60° . .	3,818
20° . .	13,478	65° . .	2,722
25° . .	12,557	70° . .	1,778
30° . .	11,484	75° . .	1,016
35° . .	10,287	80° . .	457
40° . .	9,001	85° . .	117

Air was one of the four elements of the ancient philosophers, and their opinion of its nature prevailed generally, till its accuracy was rendered questionable by the experiments of Boyle, Hooke, and Mayow. The discovery of oxygen gas in 1774 paved the way to the knowledge of its real composition, which was discovered about the same time by Scheele and Lavoisier. The former exposed some atmospheric air to a solution of sulphuret of potassium, which gradually absorbed the whole of the oxygen. Lavoisier effected the same object by the combustion of iron wire and phosphorus.

The earlier analysis of the air did not agree very well with each other. According to the researches of Lavoisier, it is composed of

27 measures of oxygen and 73 of nitrogen. The analysis of Scheele gave a somewhat higher proportion of oxygen. Priestley found that the quantity of oxygen varies from 20 to 25 per cent; and Cavendish estimated it only at 20. These discrepancies must have arisen from imperfections in the mode of analysis; for the proportion of oxygen has been found by subsequent experiments to be almost, if not exactly, that which was stated by Cavendish. The results of Scheele and Priestley are clearly referrible to this cause. It is now known that the processes they employed cannot be relied on, unless certain precautions are taken of which those chemists were ignorant. Recently boiled water absorbs nitrogen; and, consequently, if sulphuret of potassium be dissolved in that liquid by the aid of heat, the solution, when agitated with air, takes up a portion of nitrogen, and thereby renders the apparent absorption of oxygen too great. This inconvenience may be avoided by dissolving the sulphuret in cold unboiled water. Binocide of nitrogen, employed by Priestley, removes all the oxygen in the course of a few seconds; but for reasons which will soon be mentioned, its indications are apt to be fallacious. The combustion of phosphorus, as well as the gradual oxidation of that substance, acts in a very uniform manner, and removes the whole of the oxygen completely. The residual nitrogen contains a little of the vapour of phosphorus, which increases the bulk of that gas by 1-40th, for which an allowance must be made in estimating the real quantity of nitrogen.

Since chemists have learned the precautions to be taken in the analysis of the air, a close correspondence has been observed in the results of their experiments upon it. The researches of Davy, Dalton, Gay-Lussac, Thomson, and others, leave no doubt that 100 measures of pure atmospheric air consist of 20 or 21 volumes of oxygen, and 80 or 79 of nitrogen. The most approved mode of analysis consists in mixing with the air a quantity of hydrogen sufficient to convert all the oxygen present into water, and kindling the mixture by the electric spark. The combination may also be effected without detonation by means of spongy platinum. Water is formed, and is condensed; and since that liquid is composed of one volume of oxygen and two of hydrogen, one-third of the diminution must give the exact quantity of oxygen. This process is so easy of execution, and so uniform in its indications, that it is now employed nearly to the total exclusion of all others.

Such is the constitution of pure atmospheric air. But the atmosphere is never absolutely pure; for it always contains a certain variable quantity of carbonic acid and watery vapour, besides the odoriferous matter of flowers and other volatile substances, which are also frequently present. Saussure found carbonic acid in air collected at the top of Mont Blanc; and it exists at all altitudes which have been hitherto attained. Saussure, in a recent essay, states the proportion of this gas to vary at the same place within short intervals of time. It is greater in summer than in winter; and from observations made during spring, summer, and autumn, in the open fields and in calm weather, its proportion is inferred to be always greater at night than in the day, and to be more abundant in gloomy than in bright weather. A very moist state of the ground, as after much rain, diminishes the quantity of carbonic acid, apparently by direct absorption. It is rather more abundant in elevated situations, as on the summits of high mountains, than in the plains; but its quantity is there nearly the same in day and night, in wet and dry weather, because the higher strata of the air are less influenced by vegetation, and the state of the soil. Saussure thinks also that a highly electrical state of the atmosphere tends to diminish the quantity of carbonic acid. He found that 10,000 parts of air contain 4.9 of carbonic acid as a mean, 6.2 as a maximum, and 3.7 as a minimum. (*An. de Ch. et Ph.* xxxviii. 411. xlv. 5.)

The chief chemical properties of the atmosphere are owing to the presence of oxygen gas. Air from which this principle has been withdrawn is nearly inert. It can no longer support respiration and combustion, and metals are not oxidized by being heated in it. Most of the spontaneous changes which mineral and dead organized matters undergo, are owing to the powerful affinities of oxygen. The uses of the nitrogen are in a great measure unknown. It was supposed to act as a mere diluent to the oxygen; but it most probably serves some useful purpose in the economy of animals, the exact nature of which has not been discovered.

The knowledge of the composition of the air, and of the importance of oxygen to the life of animals, naturally gave rise to the notion that the healthiness of the air, at different times, and in different places, depends on the relative quantity of this gas. It was therefore supposed that the purity of the atmosphere, or its fitness for communicating health and vigour, might be discovered

by determining the proportion of oxygen; and hence the origin of the term *Eudiometer*, which was applied to the apparatus for analyzing the air. But this opinion, though at first supported by the discordant results of the earlier analysts, was soon proved to be fallacious. On the contrary, the composition of the air is not only constant in the same place, but is the same in all regions of the earth, and at all altitudes. Air collected at the summit of the highest mountains, such as Mont Blanc and Chimborazo, contains the same proportion of oxygen as that of the lowest valleys. The air of Egypt was found by Berthollet to be similar to that of France. The air which Gay-Lussac brought from an altitude of 21,735 feet above the earth, had the same composition as that collected at a short distance from its surface. Even the miasms of marshes, and the effluvia of infected places, owe their noxious qualities to some principle of too subtle a nature to be detected by chemical means, and not to a deficiency of oxygen. Seguin examined the infectious atmosphere of an hospital, the odour of which was almost intolerable, and could discover no appreciable deficiency of oxygen, or other peculiarity of composition.

The question has been much discussed, whether the oxygen and nitrogen gases of the atmosphere are simply intermixed, or chemically combined with each other. Appearances are at first view greatly in favour of the latter opinion. Oxygen and nitrogen gases differ in density, and therefore it might be expected, were they merely mixed together, that the oxygen as the heavier gas ought, in obedience to the force of gravity, to collect in the lower regions of the air; while the nitrogen should have a tendency to occupy the higher. But this has nowhere been observed. If air be confined in a long tube, preserved at perfect rest, its upper part will contain just as much oxygen as the lower, even after an interval of many months; nay, if the lower part of it be filled with oxygen, and the upper with nitrogen, these gases will be found in the course of a few hours to have mixed intimately with one another. The constituents of the air are, also, in the exact proportion for combining. By measure they are nearly in the simple ratio of 1 to 4, which agrees with the law of combination by volume; and by weight they are as 8 to 28, which corresponds to 1 eq. of oxygen and 2 of nitrogen.

Strong as are these arguments in favour of the chemical theory, it is nevertheless liable to objections which appear insuperable. The

atmosphere possesses all the characters that should arise from a mechanical mixture. There is not, as in all other cases of chemical union, any change in the bulk, form, or other qualities of its elements. The nitrogen manifests no attraction for the oxygen. All bodies which have an affinity for oxygen abstract it from the atmosphere with as much facility as if the nitrogen were absent altogether. Even water effects this separation; for the air which is expelled from rain water by ebullition, contains more than 21 per cent of oxygen. When oxygen and nitrogen gases are mixed together in the ratio of 1 to 4, the mixture occupies precisely 5 volumes, and has every property of pure atmospheric air. The refractive power of the atmosphere is precisely such as a mixture of oxygen and nitrogen gases ought to possess; and different from what would be expected were its elements chemically united. (Edinburgh Journal of Science, iv. 211.)

Since the elements of the air cannot be regarded as in a state of actual combination, it is necessary to account for the steadiness of their proportion on some other principle. It has been conceived that the affinity of oxygen and nitrogen for one another, though insufficient to cause their combination when mixed together at ordinary temperatures, might still operate in such a manner as to prevent their separation; that a certain degree of attraction is even then exerted between them, which is able to counteract the tendency of gravity. An opinion of this kind was advanced by Berthollet, in his *Statique Chimique*, and defended by Murray. This doctrine, however, is not satisfactory. It is conceivable that oxygen and nitrogen may attract each other in the way supposed; and it may be admitted that this supposition explains why these two gases continue in a state of perfect mixture. But still the explanation is unsatisfactory; and for the following reason:—Dalton took two cylindrical vessels, one of which was filled with carbonic acid, the other with hydrogen gas; the latter was placed perpendicularly over the other, and a communication was established between them. In the course of a few hours hydrogen was detected in the lower vessel, and carbonic acid gas in the upper. If the upper vessel be filled with oxygen, nitrogen, or any other gas, the same phenomena will ensue: the gases will be found, after a short interval, to be in a state of mixture, and will at last be distributed equally through both vessels. Now this result cannot be ascribed to the action of affinity. Carbonic acid cannot be made to unite either with hydro-

gen, oxygen, or nitrogen; and, therefore, it is gratuitous to assert that it has an affinity for them. Some other power must be in operation, capable of producing the mixture of gases with each other, independently of chemical attraction; and if this power can cause carbonic acid to ascend through a gas which is twenty-two times lighter than itself, it will surely explain why oxygen and nitrogen gases, the densities of which differ so little, should be intermingled in the atmosphere.

The explanation which Dalton has given of these phenomena is founded on the assumption, that the particles of one gas, though highly repulsive to each other, do not repel those of a different kind. Hence one gas should act as a vacuum with respect to another; and if a vessel full of carbonic acid communicate with another of hydrogen, the particles of each gas should insinuate themselves between the particles of the other, till they are equally diffused through both vessels. The particles of the carbonic acid do not indeed fill the space occupied by the hydrogen with the same velocity as if it were a real vacuum, because the particles of the hydrogen afford a mechanical impediment to their progress. The ultimate effect, however, is the same as if the vessel of hydrogen had been a vacuum. (Manchester Memoirs, vol. v.)

Though it would not be difficult to find objections to this hypothesis, it has the merit of being applicable to every possible case; which cannot, I conceive, be admitted of the other. It accounts not only for the mixture of gases, but for the equable diffusion of vapours through gases, and through each other. This view receives support from Graham's experiments on the diffusion of gases. (Phil. Trans. Edin. 1831.) When a gas is contained in a glass bell jar which has a crack or fissure in its sides, or communicates with the air by a narrow aperture, or is contained in a porous vessel, the gas gradually diffuses itself into the air, and air into the gas, each passing through the chink or other small opening at the same time, but in opposite directions. On ascertaining after an interval how much gas has escaped from, and how much air entered into, the vessel, it will be found that the respective quantities depend on the relative sp. gravities; and the same principle of intermixture equally applies when the apertures of communication are large, as when they are small. Each gas has a diffusiveness peculiar to itself, and which is greater as its sp. gr. is less. Graham determined the rate of diffusion for different gases by means of what he calls a *diffu-*

sion tube, which is simply a graduated tube closed at one end by plaster of Paris, a substance, when moderately dry, possessed of the requisite porosity. He has been led by direct experiment to the following conclusion,—that “the diffusion or spontaneous intermixture of two gases in contact, is effected by an interchange in position of indefinitely small volumes of the gases, which volumes are not necessarily of equal magnitude, being, in the case of each gas, inversely proportional to the square root of the density of that gas.” The relative diffusiveness of each gas may hence be represented by the reciprocal of the square root of its sp. gr. Thus, the sp. gr. of air being 1, its diffusiveness is 1 also; that of hydrogen is

$$\frac{1}{\sqrt{0.069}} = \frac{1}{0.2627} = 3.807; \text{ that of oxygen } \frac{1}{\sqrt{1.102}} = \frac{1}{1.05} = 0.9524;$$

$$\text{and that of nitrogen } \frac{1}{\sqrt{0.972}} = 1.014;$$

so that the relative power of diffusion of air, hydrogen, oxygen, and nitrogen, is indicated by the numbers, 1, 3.807, 0.9524 and 1.014. In gases which are very sparingly soluble in water, and hence not condensible by the moisture of the plaster of Paris, the results of experiment coincide so exactly with the law, that Graham suggests its application to determine the sp. gr. of gases. Thus if g denote the diffusiveness of a gas, as found by careful experiment, and d its sp. gr.; then since, by the law of diffusion,

$$g = \frac{1}{\sqrt{d}}, \text{ we have } d = \frac{1}{g^2}.$$

It is obvious that these phenomena cannot be referred to any chemical principle, but are dependent on the mechanical constitution of gases. It has been lately shown in a very clever paper by T. Thomson of Clitheroe (Phil. Mag. 3rd Series, iv. 321), that the law of gaseous diffusion is included under Dalton's hypothesis, that one gas is as a vacuum with respect to another. For it is a law deduced from the physical properties of gaseous bodies, that the velocities of gases flowing under like circumstances into a vacuum are inversely as the square roots of their sp. gravities, which is precisely the same law that regulates their flow into each other.

There is still one circumstance for consideration respecting the atmosphere. Since oxygen is necessary to combustion, to the respiration of animals, and to various other natural operations, by all of which that gas is withdrawn from the air, it is obvious that

its quantity would gradually diminish, unless the tendency of those causes were counteracted by some compensating process. To all appearance there does exist some source of compensation; for chemists have not hitherto noticed any change in the constitution of the atmosphere. The only source by which oxygen is known to be supplied, is the action of growing vegetables. A healthy plant absorbs carbonic acid during the day, appropriates the carbonaceous part of that gas to its own wants, and evolves the oxygen with which it was combined. During the night, indeed, an opposite effect is produced. Oxygen gas then disappears, and carbonic acid is eliminated; but it follows from the experiments of Priestley, Davy, and Daubeny, that plants during 24 hours yield more oxygen than they consume. Whether living vegetables make a full compensation for the oxygen removed from the air by the processes above mentioned, is uncertain. From the great extent of the atmosphere, and the continual agitation to which its different parts are subject by the action of winds, the effects of any deteriorating process would be very gradual, and a change in the proportion of its elements could be perceived only by observations made at very distant intervals.

PROTOXIDE OF NITROGEN.

Hist.—*Dephlogisticated air* of Priestley, its discoverer; and the nitrous oxide of Davy, who studied it minutely. (Researches on the Nitrous Oxide, 1800.)

Prep.—It may be formed by exposing nitric oxide for some days to the action of iron filings, or other substances which have a strong affinity for oxygen, when the nitric oxide loses one half of its oxygen, and is converted into the protoxide; but the most convenient method is by nitrate of ammonia. This salt is prepared by neutralizing with carbonate of ammonia pure nitric acid diluted with about three parts of water, and concentrating by evaporation until a drop of the liquid let fall on a cold plate becomes a firm mass, adding a little ammonia towards the close to ensure neutrality. The salt after cooling is broken to pieces, introduced into a retort, and heated by a lamp or pan of charcoal: at first, below 400°, fusion ensues; and as the heat rises to 480° or 500°, rapid decomposition sets in, which continues until all the salt disappears. If a white cloud appears within the retort, due to some of the salt subliming undecomposed, the heat should be checked.

The sole products of this operation, when carefully conducted, are water and protoxide of nitrogen. The nature of the change will be readily understood by comparing the composition of nitrate of ammonia with that of the products derived from it. These, in round numbers, are as follows :—

Nitric Acid.		Ammonia.		Water.		Prot. of Nitrogen.	
Nitrogen	14 or 1 eq.	Nitrogen	14 or 1 eq.	Hyd.	3 or 3 eq.	Nit.	28 or 2 eq.
Oxygen	40 or 5 eq.	Hydrogen	3 or 3 eq.	Oxy.	24 or 3 eq.	Oxy.	16 or 2 eq.
	<u>54</u>		<u>17</u>		<u>27</u>		<u>44</u>

The same expressed in symbols is



It thus appears that the hydrogen in the ammonia takes so much oxygen as is sufficient for forming water, and the residual oxygen converts the nitrogen both of the nitric acid and of the ammonia into protoxide of nitrogen : 71 grains of the salt will thus yield 44 grains of protoxide of nitrogen and 27 of water.

Prop.—Colourless, slightly agreeable odour, and sweetish taste; commonly gaseous, but at 45° and under a pressure of 50 atmospheres it is liquid; sp. gr. of the gas = 1.5241, and 100 C. I. weigh 47.22 grains; no action on test paper. Recently boiled water at 60° dissolves nearly its own volume of the gas, and yields it unchanged by boiling: hence it cannot be preserved over cold water, and may by it be separated from gases which are insoluble in water. It is a supporter of combustion. Most substances burn in it with far greater energy than in the atmosphere. When a recently extinguished candle with a very red wick is introduced into it, the flame is instantly restored. Phosphorus, if previously kindled, burns in it with great brilliancy. Sulphur, when burning feebly, is extinguished by it; but if immersed while the combustion is lively, the size of the flame is considerably increased. With an equal bulk of hydrogen it forms a mixture which explodes violently by the electric spark or by flame. In all these cases the product of combustion is the same as when oxygen gas or atmospheric air is used. The protoxide is decomposed; the combustible matter unites with its oxygen, and the nitrogen is set free. It suffers decomposition when a succession of electric sparks is passed through it, and a similar effect is caused by conducting it through a porcelain tube heated to incandescence. It is resolved, in both instances, into nitrogen, oxygen, and nitrous acid.

Davy discovered that it may be taken into the lungs with safety, and that it supports respiration for a few minutes. He breathed 9 quarts of it, contained in a silk bag, for three minutes, and 12 quarts for rather more than four; but no quantity could enable him to bear the privation of atmospheric air for a longer period. Its action on the system, when inspired, is very remarkable. A few deep inspirations are followed by most agreeable feelings of excitement, similar to the earlier stages of intoxication. This is shown by a strong propensity to laughter, by a rapid flow of vivid ideas, and an unusual disposition to muscular exertion. These feelings, however, soon subside; and the person returns to his usual state without experiencing the languor or depression which so universally follows intoxication from spirituous liquors. Its effects, however, on different persons, are various; and in individuals of a plethoric habit it sometimes produces giddiness, headache, and other disagreeable symptoms.

When 100 measures of it are mixed with 100 of hydrogen and fired by electricity, 100 of nitrogen gas remain, and the sole other product is water. As 100 of hydrogen unite with 50 of oxygen, it follows that 100 measures of the protoxide contain 100 of nitrogen and 50 of oxygen gases. This result, obtained by Davy, has been confirmed by Henry, who analyzed it by means of carbonic oxide gas (An. Phil. N. S. viii. 299). Now,

100 cubic inches of nitrogen gas weigh	30.166 grains
50 do. oxygen	17.054

These numbers added together amount to 47.220

which must be the weight of 100 C. I. of the protoxide. Its composition by weight is determined by the same data, being 17.054 oxygen to 30.166 nitrogen, or 8 to 14 nearly, as already stated (page 262).

Its eq. is = 22.15; eq. vol. = 100; symb. N + O, NO, or N.

BINOXIDE OF NITROGEN.

Hist.—Discovered by Hales, but first carefully studied by Priestley, under the name of *nitrous gas*. It is also called *nitric oxide*.

Prep.—Preferably by the action of nitric acid, of sp. gr. 1.2, on metallic copper. Brisk effervescence takes place without the aid of heat, and the gas may be collected over water or mercury. The copper gradually disappears during the process; the liquid acquires

a beautiful blue colour, and yields on evaporation a salt which is composed of nitric acid and oxide of copper. The chemical changes that occur are the following:—One portion of nitric acid suffers decomposition: part of its oxygen oxidizes the copper; while another part is retained by the nitrogen of the nitric acid, forming binoxide of nitrogen. The oxide of copper attaches itself to some undecomposed nitric acid, and forms the blue nitrate. Many other metals are oxidized by nitric acid, with disengagement of a similar compound; but none, mercury excepted, yields so pure a gas as copper.

Prop.—Gaseous, not hitherto condensed into a liquid; colourless, tasteless, and inodorous; excites violent spasm of the glottis when an attempt is made to inhale it; sp. gr. = 1.0377, and 100 C. I. weigh 32.137 grains. Water at 60° dissolves about .11 per cent. It has no action on test paper; but if any free oxygen is present, it produces dense, suffocating, acid vapours of a red or orange colour, called *nitrous acid vapours*, which are freely absorbed by water, and render it acid. This character distinguishes it from all other gases, and is a good test of the presence of free oxygen. In some cases it supports combustion: burning sulphur and a lighted candle are extinguished by it; but charcoal and phosphorus, when in vivid combustion, burn in it with increased brilliancy. The product of the combustion is carbonic acid in the former case, and metaphosphoric acid in the latter, nitrogen being separated in both instances. With an equal bulk of hydrogen it forms a mixture which cannot be made to explode, but which is kindled by contact with a lighted candle, and burns rapidly with a greenish white flame, water and pure nitrogen gas being the sole products. The action of freshly ignited spongy platinum on a mixture of hydrogen and binoxide of nitrogen gases leads to the slow production of water and ammonia.

It is partially resolved into its elements by being passed through red-hot tubes, and a succession of electric sparks has a similar effect. It is converted into protoxide of nitrogen by substances which have a strong affinity for oxygen, such as moist iron filings, and a solution of sulphuret of potassium. Davy ascertained its composition by the combustion of charcoal (*Elements of Chemical Philosophy*, p. 200). Two volumes of the binoxide yielded one volume of nitrogen, and about one of carbonic acid; whence it was inferred to consist of equal measures of oxygen and nitrogen gases united with-

out any condensation. Gay-Lussac (*Mémoires d'Arcueil*) proved that this proportion is rigidly exact. He decomposed 100 measures of the gas, by heating potassium in it; when 50 measures of pure nitrogen were left, and the potassa formed corresponded to 50 measures of oxygen. The same fact has been lately proved by Henry (*An. of Phil. N. S.* viii. 299). Hence, as

50 cubic inches of oxygen gas weigh	.	.	.	17·054 grains
50 do. nitrogen	.	.	.	15·083
<hr/>				<hr/>
100 cubic inches of the binoxide must weigh	.	.	.	32·137

From the invariable formation of red-coloured acid vapours, whenever binoxide of nitrogen and oxygen are mixed together, these gases detect the presence of each other with great certainty; and since the product is wholly absorbed by water, either of them may be entirely removed from any gaseous mixture by adding a sufficient quantity of the other. Priestley, who first observed this fact, supposed that combination takes place between them in one proportion only; and inferring on this supposition, that a given absorption must always indicate the same quantity of oxygen, he was led to employ binoxide of nitrogen in Eudiometry. But in this opinion he was mistaken. The discordant results obtained by his method soon excited suspicion of their accuracy; and the source of error has since been discovered by the researches of Dalton and Gay-Lussac. It appears from the experiments of Gay-Lussac, and his results do not differ materially from those of Dalton, that for 100 measures of oxygen, 400 of the binoxide may be absorbed as a maximum, and 133 as a minimum; and that between these extremes, the quantity of the binoxide corresponding to 100 of oxygen is exceedingly variable. It does not follow from this, that oxygen and binoxide of nitrogen unite in every proportion within these limits. The true explanation is, that the mixture of these gases may give rise to three compounds,—hyponitrous, nitrous, and nitric acids; and that either may be formed almost, if not entirely, to the exclusion of the others, if certain precautions are adopted. But in the usual mode of operating, two if not all are generated at the same time, and in a proportion to each other which is by no means uniform. The circumstances that influence the degree of absorption, when a mixture of oxygen and binoxide of nitrogen is made over water, are the following:—1, The diameter of the tube; 2, The rapidity with which the mixture is made;

3, The relative proportion of the two gases ; 4, The time allowed to elapse after mixing them ; 5, Agitation of the tube ; and lastly, The opposite conditions of adding the oxygen to the binoxide, or the binoxide to the oxygen.

The binoxide may, notwithstanding, be usefully employed in Eudiometry. Dalton operates (*An. of Phil.* x. 38, and *Henry's Elements*) by mixing the gases in a graduated tube about $\frac{1}{2}$ an inch wide over water, and waiting, without agitating the mixture, till decrease of volume is at an end, which usually occurs in less than 6 or 10 minutes. Every 27 measures which have disappeared, indicate 10 of oxygen. A large excess of the binoxide should be avoided ; and if the gas under examination contain more than 20 per cent. of oxygen, it should be previously diluted with nitrogen. Gay-Lussac advises that 100 measures of the gas under examination should be introduced into a very wide tube or jar, and that an equal volume of the binoxide should then be added (*Mém. d'Arcueil*, ii. 247). The red vapours, which are instantly produced, disappear very quickly ; and the absorption after half a minute, or a minute at the most, may be regarded as complete. The residue is then transferred into a graduated tube and measured. One-fourth of the loss is oxygen.—Results very near the truth may be obtained by both methods.

If a current of the binoxide be conducted into a solution of protosulphate of iron, the gas is absorbed in large quantity, and the solution acquires a deep olive-brown colour, which appears almost black when fully saturated. This solution absorbs oxygen with facility. But it cannot be safely employed in Eudiometry ; because the absorption of oxygen is accompanied, or at least very soon followed, by evolution of gas from the liquid itself. The binoxide is combined with the sulphate in the ratio of 1 eq. of the former to 4 eq. of the latter ; and the gas may be recovered by exposure to a vacuum, the original salt being left unchanged (*Paligot in An. de Ch. et Ph.* liv. 17). On applying heat, part of the gas is evolved and part decomposed : the protoxide of iron takes oxygen both from the binoxide and from water, forming peroxide of iron ; while the hydrogen of the decomposed water, and nitrogen of the binoxide combine together, and generate ammonia. Nitric acid is formed when the solution is exposed to the air or oxygen gas, but not otherwise (*Davy*). When a mixture of binoxide of nitrogen and sulphurous acid are brought into contact with a solution of potassa

or ammonia, both gases are absorbed, and a peculiar acid is generated, which has been called by Pelouze, its discoverer, *nitrosulphuric acid*. It is composed of 1 eq. of nitrogen, 1 of sulphur, and 4 of oxygen, 200 volumes of binoxide of nitrogen combining with 100 of sulphurous acid. The nitrosulphates are very prone to decomposition, a sulphate being formed with the evolution of protoxide of nitrogen: this ensues by the mere contact of certain substances, which do not themselves undergo any change, such as spongy platinum, silver and its oxide, charcoal powder, peroxide of manganese, and solutions of corrosive sublimate, lunar caustic, and the sulphates of the oxides of zinc, copper, and iron. The same effect is produced by an acid, as when an attempt is made to procure nitrosulphuric acid in a separate state, even the carbonic acid of the atmosphere being capable of causing the decomposition. The crystals of the nitrosulphates of potash and ammonia may be preserved in well-stopped bottles at ordinary temperatures; the solutions, on the contrary, are not stable above the freezing point, but the stability is much increased by an excess of alkali. On this is founded the best mode of preparing the nitrosulphates, which consists in transmitting binoxide of nitrogen through a strong solution of sulphite of ammonia or potash with an excess of alkali, when the corresponding nitrosulphate separates in colourless prismatic or acicular crystals. The dry crystals decompose at a moderate heat, namely, at 230° for the ammoniacal salt, and 266° for that of potash, the former giving rise to a slight explosion owing to the rapid evolution of protoxide of nitrogen. The decomposition of the nitrosulphate of potassa by heat is particularly interesting, from its forming sulphite of potassa and binoxide of nitrogen instead of sulphate of potassa and the protoxide, as occurs in every other instance. (Lieb. Ann. xv. 240.)

It is singular that both binoxide and protoxide of nitrogen, notwithstanding the absence of acidity, are capable of forming compounds of considerable permanence with the pure alkalies. The circumstances which give rise to the formation of these compounds will be stated in the description of nitre.

Its eq. is = 30.15 ; eq. vol. = 200 ; symb. $N + 2O$, NO_2 , or \ddot{N} .

HYPONITROUS ACID.

Hist. and Prep.—First prepared by Gay-Lussac, who showed that on adding binoxide of nitrogen in excess to oxygen gas, con-

finer in a glass tube over mercury, the absorption is always uniform, provided a strong solution of pure potassa is put into the tube before mixing the two gases: 50 measures of oxygen gas combine under these circumstances with 200 of the binoxide, forming an acid which unites with the potassa. As the binoxide contains half its volume of oxygen gas, the new acid must be composed of 100 measures of nitrogen and 150 of oxygen, as already stated (page 263). It is generated when the binoxide is kept for a considerable time, say three months, in a glass tube over mercury, with a strong solution of pure potassa, when the binoxide is resolved into hyponitrous acid, which unites with the alkali, while protoxide of nitrogen remains in the tube; and Dulong formed it by mixing 200 measures of binoxide of nitrogen with 50 of oxygen gas, both quite dry, and exposing the resulting orange fumes to intense cold, which condensed it into a liquid. It is the *nitrous* acid of Berzelius and other Continental chemists.

Prop.—At 0° it is a colourless liquid, and green at common temperatures. It is so volatile, that in open vessels the green fluid wholly and rapidly passes off in the form of an orange vapour, which is said by Mitscherlich to have a density of 1.72. On admixture with water it is converted into nitric acid and binoxide of nitrogen, the latter escaping with effervescence; but when much nitric acid is present, the hyponitrous is changed into nitrous acid, the presence of which imparts several shades of colour, orange, yellow, green, and blue, according as its quantity is more or less predominant. One eq. of hyponitrous and one of nitric acid yield two eq. of nitrous acid:—Thus $N + 3O$ and $N + 5O$ obviously contain the elements for forming $2(N + 4O)$.

Hyponitrous acid does not unite directly with alkalies, being then resolved principally into nitric acid and binoxide of nitrogen; but the hyponitrites of the alkalies and alkaline earths may be obtained by heating the corresponding nitrates to a gentle red heat; and the hyponitrite of the oxide of lead is formed by boiling a solution of the nitrate of that oxide with metallic lead.

Hyponitrous acid forms with water and sulphuric acid a crystalline compound, which is formed in large quantity during the manufacture of sulphuric acid, and the production of which is an essential part of that process. It is generated whenever moist sulphurous acid gas and nitrous acid vapour are intermixed, being instantly deposited in the form of white acicular crystals; and Gay-Lussac discovered

that it may also be made by the direct action of anhydrous nitrous and strong sulphuric acid. The first attempt to determine its composition analytically was by Henry, who found it to consist of 1 eq. of hyponitrous acid, 5 of sulphuric acid, and 5 of water. (*Ann. of Phil.* xxvii. 367.) G. De Claubry has lately repeated the analysis of the same compound in a state of more perfect dryness, and by what he considers a better method; and he gives as its constituents 2 eq. of hyponitrous acid, 4 of water, and 5 of sulphuric acid. (*An. de Ch. et Ph.* xlv. 284.) The theory of its production has been very carefully studied by De Claubry. It appears that when moist sulphurous and nitrous acids react on each other, the former is converted into sulphuric and the latter into hyponitrous acid, the oxygen lost by one being gained by the other. A little nitrogen gas is always disengaged at the same time, which can only arise from a small portion of nitrous acid losing the whole of its oxygen. The action of sulphuric on nitrous acid is different: in this case the nitrous acid is resolved into nitric and hyponitrous acids, the latter uniting with sulphuric acid and most of its water to produce the crystalline solid, while the remainder of the water unites with the nitric acid. When the crystalline matter is put into water, the hyponitrous is resolved into nitrous acid and bin-oxide of nitrogen, both of which escape with effervescence. If much water is present, more or less of the nitrous acid is converted into nitric acid and the bin-oxide. Similar changes ensue when the crystals are exposed to the air, humidity being rapidly absorbed. This subject has also been examined by Bussy with similar results.

Its eq. is = 38.15; symb. $N + 3O$, NO_2 , or \ddot{N} .

NITROUS ACID.

Prep.—It is always formed when bin-oxide of nitrogen and oxygen gases are intermixed. Davy showed, by making the mixture in a dry glass vessel previously exhausted, that nitrous acid vapour is formed by the action of 200 measures of the bin-oxide on 100 of oxygen gas; and hence, as 200 of the bin-oxide contains 100 of nitrogen and 100 of oxygen, nitrous acid was inferred to consist of 100 measures of nitrogen united with 200 of oxygen gas (page 263). This inference has been confirmed by the researches of Gay-Lussac and Dulong (*An. de Ch. et Ph.* i. and ii.), the former of whom also proved that its elements contract to 1-3rd of their volume, or in

other words, 100 measures of nitrous acid vapour contain 100 of nitrogen gas and 200 of oxygen. The specific gravity of this vapour ought to be 3.1777, formed of 0.9727 the sp. gr. of nitrogen + 2.2050 twice the sp. gr. of oxygen. It is best prepared by heating to redness in an earthen retort the nitrate of oxide of lead, carefully dried; when nitric acid is resolved into nitrous acid and oxygen, and on receiving the products in a dry tube, surrounded by a mixture of ice and salt, the former is condensed.

Prop.—An anhydrous liquid of sp. gr. 1.451, and orange colour at 60°, yellow at 32°, and almost colourless at 0°; acid, pungent, and powerfully corrosive; and imparts a yellow stain to the skin. It is very volatile, boiling at 82°: in a stopped bottle it preserves its liquid form at 60°; but when exposed to the atmosphere it is rapidly dissipated in orange red fumes, which when once mixed with air or other gases require intense cold for condensation.

Nitrous acid vapour is characterized by its orange red colour, acid reaction, and by being absorbed by water with disengagement of binoxide of nitrogen and formation of nitric acid. It is quite irrespirable, exciting great irritation and spasm of the glottis, even when moderately diluted with air. A taper burns in it with considerable brilliancy. It extinguishes burning sulphur; but the combustion of phosphorus continues in it with great vividness.

Nitrous acid is a powerful oxidizing agent, readily giving oxygen to the more oxidable metals, and to most substances which have a strong affinity for it. The acid is decomposed at the same time, being commonly changed into binoxide of nitrogen, though sometimes the protoxide and even pure nitrogen gases are evolved. When transmitted through a red-hot porcelain tube it suffers decomposition, and a mixture of oxygen and nitrogen gases is obtained.

When nitrous acid is mixed with a considerable quantity of water, it is instantly resolved into nitric acid, which unites with the water, and binoxide of nitrogen which escapes with effervescence. Three eq. of nitrous acid yield two eq. of nitric acid and one of the binoxide; for $3(N + 4O)$ contain $2(N + 5O)$ and $N + 2O$. When a rather small quantity of water is used, the evolved binoxide, at first considerable, becomes less and less as successive quantities of nitrous acid are added, till at last the evolution of gas ceases altogether. The colour of the solution varies remarkably during the process: from being colourless, the liquid acquires a blue tint, then passes into bluish green, green, yellow, and

lastly orange. These different solutions contain different relative quantities of nitric acid, nitrous acid, and water, on which circumstance the varying shades of colour depend. Nitric and nitrous acids are disposed to unite with each other, and the influence of this attraction enables nitrous acid to sustain admixture with water without decomposition. Strong nitric acid will unite with a considerable quantity of nitrous acid, and thereby acquires an orange red tint. In a weaker nitric acid the water decomposes part of the nitrous acid, and the colour of the solution is orange or yellow. As the strength of the nitric acid becomes weaker and weaker, the quantity of nitrous acid which it can protect from decomposition becomes less and less, and the colour of the solution varies from yellow, green, and blue, and is at length colourless. These changes may be witnessed, not only by adding successive quantities of nitrous acid to water, and thereby at length producing a strong nitric acid, but commencing with the latter, saturating it with nitrous acid, and then successively diluting with water.

When nitrous acid is mixed with a very small quantity of water, no binoxide of nitrogen is disengaged, but the liquid becomes green, like the colour of hyponitrous acid. I have repeatedly obtained a similar liquid in preparing nitrous acid from nitrate of oxide of lead, when the materials were not adequately dried; and that green liquid, when allowed to dissipate in the air, leaves some nitric acid behind. From these facts it seems probable that in the decomposition of nitrous acid by water, the first change is the conversion of nitrous into nitric and hyponitrous acids, which last is subsequently changed, when the required quantity of water is present, into nitric acid and binoxide of nitrogen. It may thus well happen that hyponitrous acid contributes to produce the varying colours above described.

Some chemists consider nitrous acid as a compound of nitric and hyponitrous acids, rather than of nitrogen and oxygen. In fact, on adding nitrous acid to an alkaline solution we obtain a nitrate and hyponitrite, a circumstance which has given rise to the notion that nitrous acid cannot act as a distinct acid.

Its eq. is 46·15; eq. vol = 100; symb. $N + 4O$, NO_4 , or N^{\dots} .

NITRIC ACID.

Hist.—If a succession of electric sparks be passed through a mixture of oxygen and nitrogen gases confined in a glass tube over

mercury, a little water being present, the volume of the gases will gradually diminish, and the water after a time will be found to have acquired acid properties. On neutralizing the solution with potassa, or what is better, by putting a solution of that alkali instead of water into the tube at the beginning of the experiment, a salt is obtained which possesses all the properties of nitrate of potassa. This experiment was performed in 1785 by Cavendish, who inferred from it that nitric acid is composed of oxygen and nitrogen, though the acid itself, under the name of *spirit of nitre*, had been long previously known. The best proportion of the gases was found to be seven of oxygen to three of nitrogen; but as some nitrous acid is always formed during the process, the exact composition of nitric acid cannot in this way be accurately determined.

Nitric acid may be formed much more conveniently by adding binoxide of nitrogen slowly over water to an excess of oxygen gas. Gay-Lussac proved that nitric acid may in this manner be obtained quite free from nitrous or hyponitrous acid; and that it is composed of 100 measures of nitrogen and 250 of oxygen, a result fully confirmed by Davy, Henry, Berzelius, and others.

Nitric acid cannot exist in an insulated state. Binoxide of nitrogen and oxygen gases never form nitric acid if mixed together when quite dry; and nitrous acid vapour may be kept in contact with oxygen gas without change, provided no water is present. The most simple form under which chemists have hitherto procured nitric acid is in solution with water; a liquid which, in its concentrated state, is the nitric acid of the pharmacopœia. By manufacturers it is better known by the name of *aqua fortis*.

The nitric acid of commerce is procured by decomposing some salt of nitric acid by means of oil of vitriol, and common nitre, as the cheapest of the nitrates, is employed for the purpose. This salt, previously well dried, is put into a glass retort, and a quantity of the strongest oil of vitriol is poured upon it. On applying heat, ebullition ensues, owing to the escape of nitric acid vapours, which must be collected in a receiver kept cold by moist cloths. The heat should be steadily increased during the operation, and continued as long as any acid vapours come over.

Chemists differ as to the best proportions for forming nitric acid. The London College recommends equal weights of nitre and oil of vitriol; and the Edinburgh and Dublin Colleges employ three parts of nitre to two of the acid. In the process of the London

College the alkali of the nitre is left as a bisulphate in the retort ; since one eq. of nitre (54 nitric acid and 47 potassa) is 100, and the nearly equal number 98 corresponds to 2 eq. of oil of vitriol, which contain 2 eq. of anhydrous sulphuric acid and 2 eq. of water. During the distillation the nitric acid passes over along with $1\frac{1}{2}$ eq. of water, and $\frac{1}{2}$ eq. of water is retained by the bisulphate of potassa. The presence of water is essential : nitric acid of 1.50 consists of real or anhydrous acid and water in the ratio of 1 to $1\frac{1}{2}$ or 2 to 3 ; and unless water in at least this proportion be supplied, a proportional quantity of nitric acid is resolved, at the moment of quitting the potassa into oxygen and nitrous acid (Phillips, in *Phil. Mag.* ii. 430). If the mixture be introduced into the retort without soiling its neck, and the heat be cautiously raised, the product will be quite free from sulphuric acid ; and therefore the second distillation from nitre, recommended in the pharmacopœia, is superfluous.

The proportions of the Edinburgh and Dublin Colleges are such, that the residual salt is a mixture of sulphate and bisulphate of potassa. The acid of the nitre does not receive from the oil of vitriol the requisite quantity of water, and hence part of it is decomposed, yielding towards the close of the operation an abundant supply of nitrous acid fumes. If the receiver be kept cool, nearly all these vapours are condensed, and the product is a mixture of nitric and nitrous acids, of a deep orange red colour, very strong and fuming, and of a greater sp. gr. though proportionally less in quantity, than that obtained by the foregoing process. The sp. gr. of the pale acid is 1.500 ; while that of the red acid is 1.520, or by previously drying the nitre and boiling the sulphuric acid, Hope states that it may be made so high as 1.54.

Some manufacturers decompose nitre with half its weight of sulphuric acid, thus employing the ingredients in the proportion of 1 eq. of each. In this case about half of the nitric acid is decomposed, and considerable loss sustained, unless the requisite quantity of water is previously mixed with the sulphuric acid, or water be placed in the receiver to condense the nitrous acid. Some of the nitre is likewise apt to escape decomposition ; and the residue, consisting of neutral sulphate, which is much less soluble than the bisulphate, is removed from the retort with difficulty.

In none of the preceding processes, not even in the first, is the product quite colourless ; for at the commencement and close of

the operation, nitrous acid fumes are disengaged, which communicate a straw yellow or an orange red tint, according to their quantity. If a very pale acid is required, two receivers should be used; one for condensing the colourless vapours of nitric acid, and another for the coloured products. The coloured acid is called *nitrous acid* by the College; but it is in reality a mixture or compound of nitric and nitrous acids, similar to what may be obtained by mixing anhydrous nitrous with colourless nitric acid. It is easy to convert the common mixed acid of the College into colourless nitric acid, by exposing the former to a gentle heat for some time, when all the nitrous acid will be expelled. But this process is rarely necessary, as the coloured acid may be substituted in most cases for that which is colourless. Where an acid of great strength is required, the former is even preferable.

Nitric acid frequently contains portions of sulphuric and hydrochloric acid. The former is derived from the acid which is used in the process, and the latter from sea-salt, which is frequently mixed with nitre. These impurities may be detected by adding a few drops of a solution of chloride of barium and oxide of silver to separate portions of nitric acid, diluted with three or four parts of distilled water. If chloride of barium cause a cloudiness or precipitate, sulphuric acid must be present; if a similar effect be produced by nitrate of oxide of silver, the presence of hydrochloric acid may be inferred. Nitric acid is purified from sulphuric acid by redistilling it from a small quantity of nitrate of potassa, with the alkali of which the sulphuric acid unites, and remains in the retort. To separate hydrochloric acid, it is necessary to drop a solution of nitrate of oxide of silver into the nitric acid as long as a precipitate is formed, and draw off the pure acid by distillation.

Prop.—A strong, highly corrosive acid; in its purest and most concentrated state a colourless liquid, of sp. gr. 1.50 or 1.510, chemically combined with water, from which it cannot be separated without decomposition, or by uniting with some other body. An acid of sp. gr. 1.50 contains 25 per cent of water, according to the experiments of Phillips, and 20.3 per cent according to those of Ure.* Nitric acid of this strength emits dense, white, suffocating vapours when exposed to the atmosphere. It attracts watery vapour from the air, whereby its density is diminished. A rise of tempera-

* See his Table in the Appendix, showing the strength of diluted acid of different densities.

ture is occasioned by mixing it with a certain quantity of water. When 58 measures of nitric acid of sp. gr. 1.5 are suddenly mixed with 42 of water, the temperature rises from 60 to 140°; and the mixture, on cooling to 60°, occupies the space of 92.65 measures instead of 100. From its strong affinity for water, it occasions snow to liquefy with great rapidity; and if the mixture is made in due proportion, intense cold will be generated. (Page 60.) It boils at 248°, and may be distilled without suffering material change. An acid of lower density than 1.42 becomes stronger by being heated; because the water evaporates more rapidly than the acid. An acid, on the contrary, which is stronger than 1.42 is weakened by the application of heat. It may be frozen by cold: the point of congelation varies with the strength of the acid. The strongest acid freezes at about 50° below zero. When diluted with half its weight of water, it becomes solid at $-1\frac{1}{2}^{\circ}$; but a little more water lowers its freezing point to -45° . It acts powerfully on oxidable substances, and is hence much employed by chemists for bringing bodies to their maximum of oxidation. Nearly all the metals are oxidized by it; and some of them, such as tin, copper, and mercury, are attacked with great violence. If flung on burning charcoal, it increases the brilliancy of its combustion in a high degree. Sulphur and phosphorus are converted into acids by its action. All vegetable substances are decomposed by it. In general the oxygen of the nitric acid enters into direct combination with the hydrogen and carbon of those compounds, forming water with the former, and carbonic acid with the latter. This happens remarkably in those compounds in which hydrogen and carbon are predominant, as in alcohol and the oils. It effects the decomposition of animal matters also. The cuticle and nails receive a permanent yellow stain when touched with it; and if applied to the skin in sufficient quantity it acts as a powerful cautery, destroying the organization of the part entirely.

When oxidation is effected through the medium of nitric acid, the acid itself is commonly converted into binoxide of nitrogen. This gas is sometimes given off nearly quite pure; but in general some nitrous acid, protoxide of nitrogen, or pure nitrogen, are evolved at the same time. The escape of nitrous acid in these cases seems owing, according to some late observations of Phillips, not so much to its direct formation, but to the binoxide at first formed acting on the nitric acid of the solution. Direct solar

light deoxidizes nitric acid, resolving a portion of it into oxygen and nitrous acid. The former escapes as gas; the latter is absorbed by the nitric acid, and converts it into the mixed nitrous acid of the shops. When the vapour of nitric acid is transmitted through red-hot porcelain tubes, it suffers complete decomposition, and a mixture of oxygen and nitrogen gases is the product.

Nitric acid may also be deoxidized by transmitting a current of binoxide of nitrogen through it. That gas, by taking oxygen from the nitric, is converted into nitrous acid; and a portion of nitric acid, by losing oxygen, passes into the same compound. The nitrous acid, thus derived from two sources, gives a colour to the nitric acid, the depth and kind of which depend on the strength of the acid. On saturating with binoxide of nitrogen four separate portions of nitric acid of sp. gr. 1.15, 1.35, 1.40, and 1.50, the colour will be blue in the first, green in the second, yellow in the third, and brownish red in the fourth; and acid of 1.05 is not coloured at all. Phillips found that acid of density 1.497 acquired a density 1.541, that is, was made stronger, by saturation with the binoxide; but those acids which become green are much weakened, because nitrous acid vapour is mechanically carried off by those portions of binoxide which pass unabsorbed through the liquid.

Tests.—All the salts of nitric acid are soluble in water, and therefore it is impossible to precipitate that acid by any reagent. The presence of nitric acid, when uncombined, is readily detected by its strong action on copper and mercury, emitting ruddy fumes of nitrous acid, and by its forming with potassa a neutral salt, which crystallizes in prisms, and has all the properties of nitre. Gold leaf is a still more delicate test. When hydrochloric acid is added to the solution of a nitrate, chlorine is disengaged, and the liquid hence acquires the property of dissolving gold leaf; but as the action of hydrochloric acid on the salts of chloric, bromic, iodic, and selenic acids likewise yields a solution capable of dissolving gold, no inference can be drawn from the experiment, unless the absence of these acids shall have been previously demonstrated. Another character which may be useful is to mix the supposed nitric acid or nitrate with dilute sulphuric acid in a tube, add a few fragments of pure zinc, and set fire to the hydrogen as it issues: if nitric acid be present, the flame of the hydrogen will have a greenish white tint, due to admixture with binoxide of nitrogen. This test occurred to my assistant, Mr. Balmain; and Mr.

Mr. Maitland at the same time proposed alcohol instead of zinc with the same intention. A very delicate test has been proposed by O'Shaugnessy, founded on the orange red followed by a yellow colour, which nitric acid communicates to morphia. The supposed nitrate is heated in a test tube with a drop of sulphuric acid, and then a crystal of morphia is added. (Lancet, 1829-30.) It is advisable to try the process in a separate tube with the sulphuric acid alone, in order to prove the absence of nitric acid.

SECTION VI.

CARBON.

Hist. and Prep.—It occurs pure and crystallized in forms of the octohedral system in the diamond, a mineral of unknown origin, but probably derived from the slow decomposition of vegetable matter. It is sometimes a constituent of the rocks in the form of small tabular crystals called graphite, and in larger masses mixed with iron, as plumbago with which pencils are made, and in anthracite mixed with earth and metallic sulphurets. It is the essential principle of the different varieties of charcoal—the black mass left when most vegetable and animal matters are heated to redness in close vessels, and which contains any fixed principles originally present in its source. Common charcoal is made from wood and contains about 1-50th of its weight of alkaline and earthy salts, which constitute the ashes when wood-charcoal is burned. Coke is the charcoal from coal, ivory black or animal charcoal is that from bones, lamp-black from resin. Very pure varieties of charcoal may be formed from spirit of wine, turpentine, sugar, and starch.

Prop.—Carbon, as it exists in the diamond, is the hardest substance in nature; sp. gr. 3.52; it crystallizes in the regular system in forms which are frequently hemihedral, and are characterized by a perfect cleavage parallel to the faces of the octohedron; beautifully transparent and a powerful refractor of light; a non-conductor of heat and electricity. It is very unchangeable, resists the action of acids and alkalis, and bears the most intense heat in close vessels without fusing or undergoing any perceptible change. Heated to redness in the open air, it is entirely consumed. Newton first suspected it to be combustible from its great refracting power, a conjecture which was rendered probable by the experiments of the

Florentine academicians in 1694. Lavoisier first proved it to contain carbon by throwing the sun's rays, concentrated by a powerful lens, upon a diamond contained in a vessel of oxygen gas. The diamond was consumed entirely, oxygen disappeared, and carbonic acid was generated. It has since been demonstrated by the researches of Guyton-Morveau, Smithson Tennant, Allen and Pepys, and Davy, that carbonic acid is the product of its combustion. Guyton-Morveau inferred from his experiments that the diamond is pure carbon, and that charcoal is an oxide of carbon. Tennant burned diamonds by heating them with nitre in a gold tube; and comparing his own results with those of Lavoisier on the combustion of charcoal, he concluded that equal weights of diamond and pure charcoal, in combining with oxygen, yield precisely equal quantities of carbonic acid. He was thus induced to adopt the opinion, that charcoal and the diamond are chemically the same substance; and that the difference in their physical character is solely dependant on a difference of aggregation.* This conclusion was confirmed by the experiments of Allen and Pepys†, and Davy‡, who compared the product of the combustion of the diamond with that derived from different kinds of charcoal. The latter chemist did indeed observe the production of a minute quantity of water during the combustion of the purest charcoal, indicative of a trace of hydrogen; but its quantity is so small, that it cannot be regarded as a necessary constituent. It proves only that a trace of hydrogen is retained by charcoal with such force, that it cannot be expelled by the temperature of ignition.

Charcoal, as obtained from wood, is hard and brittle, conducts heat very slowly, but is a good conductor of electricity; quite insoluble in water, is attacked with difficulty by nitric acid, and is little affected by any of the other acids, or by the alkalies. It undergoes little change from exposure to air and moisture, being less injured under these circumstances than wood. It is exceedingly refractory in the fire, if excluded from the air, supporting the most intense heat which chemists are able to produce without change.

It possesses the property of absorbing a large quantity of air or other gases at common temperatures, and of yielding the greater part of them again when it is heated. It appears from the researches of Saussure, that different gases are absorbed by it in different proportions. His experiments were performed by plunging a piece of

* Phil. Trans. 1797.

† Ibid. 1807.

‡ Ibid. 1814.

red-hot charcoal under mercury, and introducing it when cool into the gas to be absorbed. He found that charcoal prepared from box-wood absorbs, during the space of 24 or 36 hours, of

Ammoniacal gas	.	.	.	90 times its volume.
Muriatic acid	.	.	.	85
Sulphurous acid	.	.	.	65
Sulphuretted hydrogen	.	.	.	81 (Dr. C. Henry.)
Nitrous oxide	.	.	.	40
Carbonic acid	.	.	.	35
Olefiant gas	.	.	.	35
Carbonic oxide	.	.	.	9.42
Oxygen	.	.	.	9.25
Nitrogen	.	.	.	7.5
Hydrogen	.	.	.	1.75

The absorbing power of charcoal, with respect to gases, cannot be attributed to chemical action; for the quantity of each gas, which is absorbed, bears no relation whatever to its affinity for charcoal. The effect is in reality owing to the peculiar porous texture of that substance, which enables it, in common with most spongy bodies, to absorb more or less of all gases, vapours, and liquids with which it is in contact. This property is most remarkable in charcoal prepared from wood, especially in the compact varieties of it, the pores of which are numerous and small. It is materially diminished by reducing the charcoal to powder; and in plumbago, which has not the requisite degree of porosity, it is wanting altogether.

The porous texture of charcoal accounts for the general fact of absorption only; its power of absorbing more of one gas than of another, must be explained on a different principle. This effect, though modified to all appearance by the influence of chemical attraction, seems to depend chiefly on the natural elasticity of the gases. Those which possess such a great degree of elasticity as to have hitherto resisted all attempts to condense them into liquids, are absorbed in the smallest proportion; while those that admit of being converted into liquids by compression, are absorbed more freely. For this reason, charcoal absorbs vapours more easily than gases, and liquids than either.

Allen and Pepys determined experimentally the increase in weight experienced by different kinds of charcoal, recently ignited, after a week's exposure to the atmosphere. The charcoal from fir gained 13 per cent.; that from *lignum vitæ*, 9.6; that from box, 14; from beech, 16.3; from oak, 16.5; and from mahogany, 18. The absorption is most rapid during the first 24 hours. The substance absorbed is both water and atmospheric air, which the char-

coal retains with such force, that it cannot be completely separated from them without exposure to a red heat. Vogel has observed that charcoal absorbs oxygen in a much greater proportion from the air than nitrogen. Thus, when recently ignited charcoal, cooled under mercury, was put into a jar of atmospheric air, the residue contained only 8 per cent. of oxygen gas; and if red-hot charcoal be plunged into water, and then introduced into a vessel of air, the oxygen disappears almost entirely. It is said that pure nitrogen may be obtained in this way. (Schweigger's Journal, iv.)

Charcoal likewise absorbs the odoriferous and colouring principles of most animal and vegetable substances. When coloured infusions of this kind are digested with a due quantity of charcoal, a solution is obtained, which is nearly if not quite colourless. Tainted flesh may be deprived of its odour by this means, and foul water be purified by filtration through charcoal. The substance commonly employed to decolorize fluids is animal charcoal reduced to a fine powder. It loses the property of absorbing colouring matters by use, but recovers it by being heated to redness.

Charcoal is highly combustible. When strongly heated in the open air, it takes fire, and burns slowly. In oxygen gas, its combustion is lively, and accompanied with the emission of sparks. In both cases it is consumed without flame, smoke, or residue, if quite pure; and carbonic acid gas is the product of its combustion.

Its eq. is = 6.12; its vapour (theoretical, p. 231) has a sp. gr. = 0.4215, and eq. vol. = 100, and 100 C. I. weigh 13.153 grains.

The composition of the compounds of carbon described in this section is as follows:—

	Carbon.		Oxygen.		Equiv.	Formulae.
Carbonic Oxide	6.12 or 1 eq.	+	8 or 1 eq.	=	14.12	C+O or C̄.
Carbonic Acid	6.12 or 1 eq.	+	16 or 2 eq.	=	22.12	C+2O or C̄.

Carbonic oxide gas is theoretically considered as a compound of 100 measures of the vapour of carbon and 50 of oxygen condensed into 100 measures; and carbonic acid gas, of 100 measures of the vapour of carbon and 100 of oxygen condensed into 100 measures.

CARBONIC ACID.

Hist.—Discovered by Black in 1757, and described by him in his inaugural dissertation on magnesia under the name of *fixed air*. He observed the existence of this gas in common limestone and

magnesia, and found that it may be expelled from these substances by the action of heat or acids. He also remarked that the same gas is formed during respiration, fermentation, and combustion. Its composition was first demonstrated synthetically by Lavoisier, who burned carbon in oxygen gas, and obtained carbonic acid as the product. The same experiment has been repeated by Davy, Allen and Pepys, and others, with the result that in the combustion of diamond or other pure carbonaceous matter the oxygen undergoes no change of volume, or in other words, that carbonic acid gas contains its own volume of oxygen: hence the difference of the sp. gravities of carbonic acid and oxygen gases ($1.524 - 1.1025$), or 0.4215 , gives the exact ratio of the quantities of carbon and oxygen combined, being 0.4215 to 1.1025 , or 6.12 to 16 . Smithson Tennant illustrated its nature analytically by passing the vapour of phosphorus over chalk, or carbonate of lime, heated to redness in a glass tube. The phosphorus took oxygen from the carbonic acid, charcoal in the form of a light black powder was deposited, and the phosphoric acid, which was formed, united with the lime.

Prep.—Conveniently by the action of hydrochloric acid, diluted with two or three times its weight of water, on fragments of marble, when carbonic acid gas escapes with effervescence, and chloride of calcium is left in solution.

Prop.—Commonly a colourless gas of a pungent odour and acidulous taste, condensable at 32° by a pressure of 36 atmospheres into a liquid, which congeals by the cold produced by its own evaporation, estimated at -180° , and at that temperature is solid under the atmospheric pressure, being the first instance of a solidified gas. The sp. gr. of the gas is 1.524 , and 100 C. I. at 60° and 30 Bar. weigh 47.262 grains; the sp. gr. of the liquid at 32° is 0.83 ; it dilates remarkably from heat, its expansion being upwards of four times that of air, 20 volumes of the liquid at 32° occupying 29 volumes at 86° , and its sp. gr. varies from 0.9 to 0.6 as the temperature rises from -4° to $+86^{\circ}$. When heated from 32° to 86° its elasticity rises from 36 to 73 atmospheres, being 0.68 atmospheres for each degree. It is insoluble in water and fat oils, but soluble in all proportions in ether, alcohol, naphtha, oil of turpentine, and bisulphuret of carbon. The evaporation of its ethereal solution causes an intense degree of cold, by which large quantities of mercury may be frozen. (Theloirier in Ann. de Ch. et Ph. lx. 427.)

Carbonic acid gas extinguishes burning substances of all kinds,

and the combustion does not cease from the want of oxygen only. It exerts a positive influence in checking combustion, as appears from the fact, that a candle cannot burn in a gaseous mixture composed of four measures of atmospheric air, and one of carbonic acid.

It is not better qualified to support the respiration of animals; for its presence, even in moderate proportion, is soon fatal. An animal cannot live in air which contains sufficient carbonic acid for extinguishing a lighted candle; and hence the practical rule of letting down a burning taper into old wells or pits before any one ventures to descend. If the light is extinguished, the air is certainly impure; and there is generally thought to be no danger, if the candle continues to burn. But some instances have been known of the atmosphere being sufficiently loaded with carbonic acid to produce insensibility, and yet not so impure as to extinguish a burning candle. (Christison on Poisons, 2nd ed. 707.) When an attempt is made to inspire pure carbonic acid, violent spasm of the glottis takes place, which prevents the gas from entering the lungs. If it be so much diluted with air as to admit of its passing the glottis, it then acts as a narcotic poison on the system. It is this gas which has often proved destructive to persons sleeping in a confined room with a pan of burning charcoal.

It is quite incombustible, and cannot be made to unite with an additional portion of oxygen. It is a compound, therefore, in which carbon is in its highest degree of oxidation.

Lime water becomes turbid when brought into contact with carbonic acid. The lime unites with the gas, forming carbonate of lime, which, from its insolubility in water, at first renders the solution milky, and afterwards forms a white flaky precipitate. Hence lime water is not only a valuable test of the presence of carbonic acid, but is frequently used to withdraw it altogether from any gaseous mixture that contains it.

Recently boiled water dissolves its own volume of carbonic acid gas at 60° and 30 Bar.; but it will take up much more if the pressure be increased. The quantity of the gas absorbed is in exact ratio with the compressing force; that is, water dissolves twice its volume when the pressure is doubled, and three times its volume when the pressure is trebled. A saturated solution may be made by transmitting a stream of the gas through a vessel of cold water during the space of half an hour, or still better by the use of a Woulfe's bottle or Nouth's apparatus, so as to aid the absorption

by pressure. Water and other liquids which have been charged with carbonic acid under great pressure, lose the greater part of the gas when the pressure is removed. The effervescence which takes place on opening a bottle of ginger beer, cider, or brisk champaign, is owing to the escape of carbonic acid gas. Water, if fully saturated with carbonic acid gas, sparkles when it is poured from one vessel into another. The solution has an agreeably acidulous taste, and gives to litmus paper a red stain which is lost on exposure to the air. On the addition of lime water to it, a cloudiness is produced, which at first disappears, because the carbonate of lime is soluble in excess of carbonic acid; but a permanent precipitate ensues when the free acid is neutralized by an additional quantity of lime water. The water which contains carbonic acid in solution is wholly deprived of the gas by boiling. Removal of pressure from its surface by means of the air-pump has a similar effect.

The agreeable pungency of beer, porter, and ale, is in a great measure owing to the presence of carbonic acid; by the loss of which, on exposure to the air, they become stale. All kinds of spring and well water contain carbonic acid absorbed from the atmosphere, and to which they are partly indebted for their pleasant flavour. Boiled water has an insipid taste from the absence of carbonic acid.

Carbonic acid is always present in the atmosphere, even at the summit of the highest mountains, or at a distance of several thousand feet above the ground. Its presence may be demonstrated by exposing lime water in an open vessel to the air, when its surface will soon be covered with a pellicle, which is carbonate of lime. The origin of the carbonic acid is obvious. Besides being formed abundantly by the combustion of all substances which contain carbon, the respiration of animals is a fruitful source of it, as may be proved by breathing for a few minutes into lime water; and it is also generated in all the spontaneous changes to which dead animal and vegetable matters are subject. The carbonic acid proceeding from such sources, is commonly diffused equably through the air; but when any of these processes occur in low confined situations, as at the bottom of old wells, the gas is then apt to accumulate there, and form an atmosphere called *choke damp*, which is fatal to any animals that are placed in it. These accumulations happily never take place, except when there is some local origin for the carbonic acid; as, for example, when it is generated by fermentative pro-

cesses going on at the surface of the ground, or when it issues directly from the earth, as happens at the Grotto del Cane in Italy, and at Pyrmont in Westphalia. There is no real foundation for the opinion that carbonic acid can separate itself from the great mass of the atmosphere, and accumulate in a low situation merely by the force of gravity. Such a supposition is contrary to the well-known tendency of gases to diffuse themselves equally through each other. It is also contradicted by observation; for many deep pits, which are free from putrefying organic remains, though otherwise favourably situated for such accumulations, contain pure atmospheric air.

Though carbonic acid is the product of many natural operations, chemists have not hitherto noticed any increase in the quantity contained in the atmosphere. The only known process which tends to prevent increase in its proportion, is that of vegetation. Growing plants purify the air by withdrawing carbonic acid, and yielding an equal volume of pure oxygen in return; but whether a full compensation is produced by this cause, has not yet been satisfactorily determined.

Carbonic acid is contained in the earth. Many mineral springs, such as those of Tunbridge, Pyrmont, and Carlsbad, are highly charged with it. In combination with lime it forms extensive masses of rock, which geologists have found to occur in all countries, and in every formation.

Carbonic acid unites with alkaline substances, and the salts so constituted are called *carbonates*. Its acid properties are feeble, so that it is unable to neutralize completely the alkaline properties of potassa, soda, and lithia. For the same reason, all the carbonates, without exception, are decomposed by the hydrochloric and all the stronger acids; when carbonic acid is displaced, and escapes in the form of gas.

Its eq. is 22.12; eq. vol = 100; symb. C + 2O, CO₂, or \ddot{C} .

CARBONIC OXIDE GAS.

Hist.—Priestley discovered it by igniting chalk in a gun-barrel, and afterwards obtained it by heating a mixture of chalk and iron filings. He supposed it to be hydrogen mixed with carbonic acid. Its real nature was pointed out by Cruickshank (Nicholson's Journal, 4to ed. v.), and about the same time by Clément and Désormes (An. de Chimie, xxxix.).

Prep.—1. By transmitting carbonic acid gas over red-hot fragments of charcoal contained in a tube of iron or porcelain. 2. By igniting alkaline or earthy carbonates with iron filings, charcoal, or some deoxidizing substance. 3. By heating binoxalate of potassa with five or six times its weight of strong oil of vitriol in a retort. Effervescence soon ensues, owing to the escape of gas consisting of equal measures of carbonic acid and carbonic oxide gases; and on absorbing the former by an alkaline solution, the latter is left in a state of perfect purity. To comprehend the theory of the process it is necessary to premise, that oxalic acid is a compound of equal measures of carbonic acid and carbonic oxide, or at least its elements are in the proportion to form these gases; and that it cannot exist unless in combination with water or some other substance. Now the sulphuric acid unites both with the potassa and water of the binoxalate, and the oxalic acid being thus set free, is instantly decomposed. Oxalic acid may be substituted in this process for binoxalate of potassa.

Prop.—A colourless, inodorous gas; sp. gr. = 0.9727, and 100 C. I. at 60° and 30 Bar. weigh 30.207 grains; has neither acid nor alkaline properties; is sparingly dissolved by water, and does not render lime water turbid. It is inflammable. When a lighted taper is plunged into it, the taper is extinguished; but the gas itself is set on fire, and burns calmly at its surface with a lambent blue flame. The sole product of its combustion, when the gas is quite pure, is carbonic acid, a fact which proves that it does not contain any hydrogen. It cannot support respiration. It acts injuriously on the system; for if diluted with air, and taken into the lungs, it very soon occasions headache and other unpleasant feelings; and when breathed pure, it almost instantly causes profound coma.

A mixture of carbonic oxide and oxygen gases may be made to explode by flame, by a red-hot solid body, or by the electric spark. If mixed together in the ratio of 100 measures of carbonic oxide and rather more than 50 of oxygen, and the mixture is inflamed in Volta's Eudiometer by electricity so as to collect the product of the combustion, the whole of the carbonic oxide, together with 50 measures of oxygen, disappears, and 100 measures of carbonic acid gas occupy their place. From this fact, first ascertained by Berthollet, and since confirmed by subsequent observation, it follows that carbonic oxide contains half as much oxygen, and as much

carbon, as carbonic acid. Accordingly its density should be 0.4215 (sp. gr. of carbon vapour) $+0.5512$ (half the sp. gr. of oxygen gas) $= 0.9727$, which is the number found experimentally by Dulong and Berzelius.

The two first processes mentioned for generating carbonic oxide will now be intelligible. The principle of the methods is to bring carbonic acid at a red heat in contact with some substance which has a strong affinity for oxygen. This condition is fulfilled by igniting chalk, or any carbonate which can bear a red heat without decomposition, such as the carbonates of baryta, strontia, soda, potassa, or lithia, with half its weight of iron filings or charcoal. The carbonate is reduced to the caustic state, and its carbonic acid is converted into carbonic oxide by yielding oxygen to the iron or charcoal. When the former is used, oxide of iron is the product; when charcoal is employed, the charcoal itself is oxidized, and yields carbonic oxide. This gas may likewise be generated by heating to redness a mixture of almost any metallic oxide with one-sixth of its weight of charcoal powder. The oxides of zinc, iron, or copper, are the cheapest and most convenient. In all these processes it is essential that the ingredients be quite free from moisture and hydrogen, otherwise some carburetted hydrogen gas would be generated. The product should always be washed with lime water to separate it from carbonic acid.

Henry has ascertained that when a succession of electric sparks is passed through carbonic acid confined over mercury, a portion of that gas is converted into carbonic oxide and oxygen. When a mixture of hydrogen and carbonic acid gases is electrified, a portion of the latter yields one half of its oxygen to the former; water is generated, and carbonic oxide produced. On electrifying a mixture of equal measures of carbonic oxide and protoxide of nitrogen, both gases are decomposed without change of volume, and the residue consists of equal measures of carbonic acid and nitrogen gases. The carbonic oxide should be in very slight excess, in order to ensure the success of the experiment. On this fact is founded Henry's method of analyzing protoxide of nitrogen, and testing its purity, as will be more particularly mentioned in the fourth part of the work.

Its eq. is 14.12 ; eq. vol. $= 100$; symb. $C + O$, CO , or \dot{C} .

SECTION VII.

SULPHUR.

Hist.—It occurs as a mineral production in some parts of the earth, particularly in the neighbourhood of volcanoes, as in Italy and Sicily. It is commonly found in a massive state; but it is sometimes met with crystallized in the form of a right rhombic octohedron. It exists much more abundantly in combination with several metals, such as silver, copper, antimony, lead, and iron. It is procured in large quantity by exposing iron pyrites to a red heat in close vessels.

Prop.—A nearly tasteless, brittle solid; colour greenish yellow; odour when rubbed peculiar; sp. gr. 1.99; non-conductor of electricity and heat. Its point of fusion is 232° ; between 232° and 280° it possesses the highest degree of fluidity, is then of an amber colour, and if cast into cylindrical moulds, forms the common roll sulphur of commerce. It begins to thicken near 320° , and acquires a reddish tint; and at temperatures between 428° and 482° , it is so tenacious that the vessel may be inverted without causing it to change its place. From 482° to its boiling point it again becomes liquid, but never to the same extent as when at 248° . When heated to at least 428° , and then poured into water, it becomes a ductile mass, which may be used for taking the impression of seals.

Fused sulphur has a tendency to crystallize in cooling. A crystalline arrangement is perceptible in the centre of common roll sulphur; and by good management regular crystals may be obtained. For this purpose several pounds of sulphur should be melted in an earthen crucible; and when partially cooled, the outer solid crust should be pierced, and the crucible quickly inverted, so that the inner and as yet fluid parts may gradually flow out. On breaking the solid mass, when quite cold, crystals of sulphur will be found in its interior.

Sulphur is very volatile. It begins to rise slowly in vapour even before it is completely fused. At 550° or 600° it volatilizes rapidly, and condenses again unchanged in close vessels. Common sulphur is purified by this process; and if the sublimation be conducted slowly, the sulphur collects in the receiver in the form of

detached crystalline grains, called *flowers of sulphur*. In this state, however, it is not quite pure; for the oxygen of the air within the apparatus combines with a portion of sulphur during the process, and forms sulphurous acid. The acid may be removed by washing the flowers repeatedly with water.

The sp. gr. of sulphur vapour was found by Dumas to lie between 6.51 and 6.617, and by Mitscherlich 6.9 (An de Ch. et Ph. lv. 8.): its sp. gr. by calculation (page 231) is 6.648. Hence, could the vapour continue as such at 60° and 30 Bar., 100 cubic inches should weigh 206.17 grains.

Sulphur is insoluble in water. It dissolves readily in boiling oil of turpentine. The solution has a reddish brown colour like melted sulphur, and if fully saturated deposits numerous small crystals in cooling. It is also soluble in alcohol, if both substances are brought together in the form of vapour. The sulphur is precipitated from the solution by the addition of water.

Sulphur, like charcoal, retains a portion of hydrogen so obstinately that it cannot be wholly freed from it either by fusion or sublimation. Davy detected its presence by exposing sulphur to the strong heat of a powerful galvanic battery, when some hydro-sulphuric acid gas was disengaged. The hydrogen, from its minute quantity, can only be regarded in the light of an accidental impurity, and as in no wise essential to the nature of sulphur.

When sulphur is heated in the open air to 300° or a little higher, it kindles spontaneously, and burns with a faint blue light. In oxygen gas its combustion is far more vivid; the flame is much larger, and of a bluish white colour. Sulphurous acid is the product in both instances;—no sulphuric acid is formed even in oxygen gas unless moisture be present.

Crystals of native sulphur, which have been formed by the condensation of sulphurous vapour, as well as those which are deposited from a solution of sulphur in any menstruum, possess forms which are either identical, or connected by being referable to the same crystalline axes. Such, on the contrary, as are produced by the cooling of fused sulphur in the manner above described, belong to a different system of crystallization. The condition determining the form is temperature: if the crystal be formed below 232°, it belongs to the right prismatic system; if at that point, to the oblique prismatic. This is proved by the influence of temperature on a crystal of either system: a crystal of fusion when first formed

is perfectly clear and transparent, but kept at common temperatures, it soon becomes opaque, and presents the appearance of the roll sulphur of commerce: the same change occurs when a native crystal is placed in a solution of a salt which boils at 232° . The opacity is in both cases produced by a new arrangement of the particles of sulphur, by which, without any change in the exterior form, the internal structure of the crystal is altered to correspond to the crystallization peculiar to the temperature.

The eq. of sulphur is 16.1; eq. vol. 16.66; symb. S.

The compounds of sulphur described in this section are composed as follows:—

	Sulphur.	Oxygen.	Equiv.	Formulae.
Sulphurous acid	16.1 or 1 eq.	+ 16 or 2 eq.	= 32.1	S+2O or $\overset{\cdot\cdot}{\underset{\cdot\cdot}{S}}+2\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}$
Sulphuric acid	16.1 or 1 eq.	+ 24 or 3 eq.	= 40.1	S+3O or $\overset{\cdot\cdot}{\underset{\cdot\cdot}{S}}+3\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}$
Hyposulphurous acid	32.2 or 2 eq.	+ 16 or 2 eq.	= 48.2	2S+2O or $\overset{\cdot\cdot}{\underset{\cdot\cdot}{S}}_2+2\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}$
Hyposulphuric acid	32.2 or 2 eq.	+ 40 or 5 eq.	= 72.2	2S+5O or $\overset{\cdot\cdot}{\underset{\cdot\cdot}{S}}_2+5\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}$

Taking 16.66 as the eq. vol. of the vapour of sulphur, the weight of which is represented by 1.108 (page 231), these compounds, by measure, are thus constituted:—

	Sulp.	Oxy.	Cond. into.	Densities.
Sulphurous acid	16.66 + 100	100	100	$1.108 + 1.1025 = 2.2105$
Sulphuric acid	16.66 + 150	150	100	$1.108 + 1.6537 = 2.7617$
Hyposulphurous acid	33.33 + 100	100	unknown	
Hyposulphuric acid	33.33 + 250	250	unknown	

SULPHUROUS ACID.

Hist. and Prep.—Discovered as a gas by Priestley. It is the sole product of the combustion of sulphur in air or dry oxygen gas, and is freely evolved, mixed with carbonic acid, when chips of wood, straw, cork, oil, or most other organic matters are heated in strong sulphuric acid, which yields oxygen to the carbon and hydrogen of those substances, and is thereby converted into sulphurous acid. Nearly all the metals, with the aid of heat, have a similar effect: one portion of the acid yields oxygen to the metal, and is thus reduced to sulphurous acid; while the metallic oxide, at the moment of its formation, unites with sulphuric acid. A very pure gas may thus be obtained by means of copper or mercury.

Prop.—Commonly gaseous, colourless, of a pungent suffocating odour, being that emitted by burning sulphur; taste, acid; sp. gr. 2.2105, and 100 C.I. at 60° and 30 Bar. weigh 68.691 grains; it

is liquid at 45° under the pressure of two atmospheres, and at 0° under that of one atmosphere. The gas extinguishes all burning bodies which are immersed into it, and is not inflammable. It does not support respiration, but causes violent irritation and spasm of the glottis; and even when diluted with air, it excites cough when inspired, and causes a peculiar uneasiness about the chest. Water, at 60° and 30 Bar. dissolves 33 times its volume, the solution having the peculiar odour of the gas, and yielding it unchanged by ebullition. It has considerable bleaching properties: at first it reddens litmus paper, and then slowly bleaches it; but most vegetable colours, as of the rose and violet, are speedily removed by it without being first reddened. The colouring principle is not destroyed, but may be restored by a stronger acid or by an alkali.

Davy proved that sulphurous acid gas contains exactly its own volume of oxygen (Elements, p. 273), and consequently the difference in the weights or sp. gr. of these gases ($2.2105 - 1.1025 = 1.108$) gives the weight of sulphur combined with oxygen. The sulphur and oxygen are thus found to be in the ratio of 1.108 to 1.1025, or 16.1 to 16.

Liquid sulphurous acid is easily obtained by transmitting the dry pure gas through a glass tube surrounded by a freezing mixture of snow and salt. Its sp. gr. is 1.45; it boils at 14° , and from the rapidity of its evaporation causes intense cold; it conducts electricity (Kemp). When exposed to cold in the moist state, a crystalline solid is formed, which contains 20 per cent of water, and probably consists of 1 eq. of the acid to 14 eq. of water.

Though sulphurous acid cannot be made to burn by the approach of flame, it has a very strong attraction for oxygen, uniting with it under favourable circumstances, and forming sulphuric acid. The presence of moisture is essential to this change. A mixture of sulphurous acid and oxygen gases, if quite dry, may be preserved over mercury for any length of time without chemical action; but if a little water be admitted, the sulphurous acid gradually unites with oxygen, and sulphuric acid is generated. Many of the chemical properties of sulphurous acid are owing to its affinity for oxygen. The solutions of metals which have a weak affinity for oxygen, such as gold, platinum, and mercury, are completely decomposed by it, those substances being precipitated in the metallic form. Nitric acid converts it instantly into sulphuric acid by yielding some of its oxygen. Peroxide of manganese causes a simi-

lar change, and is itself converted into protoxide of manganese, which unites with the resulting sulphuric acid.

Sulphurous acid gas may be passed through red-hot tubes without decomposition. Several substances which have a strong affinity for oxygen, such as hydrogen, carbon, and potassium, decompose it at the temperature of ignition.

Sulphurous acid combines with metallic oxides, and forms salts which are called *sulphites*, which are decomposed by sulphuric acid, and then emit the characteristic odour of sulphurous acid.

Its eq. is 32.1; eq. vol. = 100; symb. S + 2O, SO₂, or S̄.

SULPHURIC ACID.

Hist. and Prep.—Sulphuric acid, or *oil of vitriol* as it is often called, was discovered by Basil Valentine towards the close of the 15th century. It is procured for the purposes of commerce by two methods. One of these has been long pursued in the manufactory at Nordhausen in Germany, and consists in decomposing sulphate of oxide of iron (green vitriol) by heat. This salt contains 6 eq. of water of crystallization; and when strongly dried by the fire, it crumbles down into a white powder, which, according to Thomson, contains 1 eq. of water. On exposing this dried proto-sulphate to a red heat, its acid is wholly expelled, the greater part passing over unchanged into the receiver, in combination with the water of the salt. Part of the acid, however, is resolved by the strong heat employed in the distillation into sulphurous acid and oxygen. The former escapes as gas throughout the whole process; the latter only in the middle and latter stages, since, in the beginning of the distillation, it unites with the protoxide of iron. Peroxide of iron is the sole residue.

The acid, as procured by this process, is a dense, oily liquid of a brownish tint. It emits copious white vapours on exposure to the air, and is hence called *fuming sulphuric acid*. Its sp. gr. is 1.896 or 1.90. According to Thomson it consists of 80 parts or 2 eq. of anhydrous acid, and 9 parts or 1 eq. of water. On putting this acid into a glass retort, to which a receiver surrounded by snow is securely adapted, and heating it gently, a transparent colourless vapour passes over, which condenses into a white crystalline solid. This substance is pure anhydrous sulphuric acid. It is tough and elastic; liquefies at 66° and boils at a temperature between 104° and 122°, forming, if no moisture is present, a transparent vapour.

Exposed to the air, it unites with watery vapour, and flies off in the form of dense white fumes. The residue of the distillation is no longer fuming, and is in every respect similar to the common acid of commerce.

The other process for forming sulphuric acid, which is practised in Britain and in most parts of the Continent, is by burning sulphur previously mixed with one-eighth of its weight of nitrate of potassa. The mixture is burned in a furnace so contrived that the current of air, which supports the combustion, conducts the gaseous products into a large leaden chamber, the bottom of which is covered to the depth of several inches with water. The nitric acid yields oxygen to a portion of sulphur, and converts it into sulphuric acid, which combines with the potassa of the nitre; while the greater part of the sulphur forms sulphurous acid by uniting with the oxygen of the air. The nitric acid, in losing oxygen, is converted, partly perhaps into nitrous acid, but chiefly into bin-oxide of nitrogen, which, by mixing with air at the moment of its separation, gives rise to the red nitrous acid vapours. The gaseous substances, present in the leaden chamber, are therefore sulphurous and nitrous acids, atmospheric air, and watery vapour. The explanation of the mode in which these substances react on each other, so as to form sulphuric acid, was suggested by the experiments of Clément and Désormes (*An. de Ch. lix.*), and Davy (*Elements*, p. 276). When dry sulphurous acid gas and nitrous acid vapour are mixed together in a glass vessel quite free from moisture, no change ensues; but if a few drops of water be added, in order to fill the space with aqueous vapour, the white crystalline compound, described at page 280, is immediately produced. Clément and Désormes believed it to consist of sulphuric acid, bin-oxide of nitrogen, and water; and Davy, of sulphurous acid, nitrous acid, and water. But the observation, that the same compound may be made with sulphuric and anhydrous nitrous acids, and that when decomposed by water both nitrous acid and bin-oxide of nitrogen are disengaged, led Gay-Lussac to the opinion which now seems to be fully substantiated by experiment. (Page 281.) A consistent account may, therefore, be given of what really takes place within the leaden chambers.—The mutual reaction of humidity, sulphurous acid, and nitrous acid, gives rise to the crystalline compound of sulphuric acid, hyponitrous acid, and water; and when this solid falls into the water of the chamber, it is instantly decom-

posed, sulphuric acid is dissolved, and nitrous acid and binoxide of nitrogen escape with effervescence. The nitrous acid thus set free, as well as that reproduced by the binoxide uniting with the oxygen of the atmosphere, is again intermixed with sulphurous acid and humidity, and thus gives rise to a second portion of the crystalline solid, which undergoes the same change as the first. A certain portion of nitric acid is usually formed by the action of water on the nitrous acid; but the presence of sulphuric acid in that water tends to prevent the free decomposition of nitrous acid which pure water produces. Nay, when the water becomes pretty strongly acid, the nitric acid at first generated is reduced, by absorbed sulphurous acid, into the hyponitrous, which unites with sulphuric acid, and remains even after concentration: it is the cause of the evolution of binoxide of nitrogen which usually ensues when common oil of vitriol is diluted, the hyponitrous acid being then decomposed by the water (Dana). When the water of the chamber is sufficiently charged with acid, it is drawn off, and concentrated by evaporation. It hence appears that the oxygen, by which the sulphurous is converted into sulphuric acid, is in reality supplied by the air; that the combination is effected, not directly, but through the medium of nitrous acid; and that a small quantity of nitrous acid is sufficient for the production of a large quantity of sulphuric acid. The decomposition of the crystalline solid by water seems owing to the strong affinity of that liquid for sulphuric acid.

Besides hyponitrous acid as above stated, it contains potassa, and the oxide of lead and sometimes iron, the first derived from the nitre employed in making it, and the two latter from the leaden chamber. To separate them, the acid should be distilled from a glass or platinum retort: the former may be safely used by putting into it some fragments of platinum leaf, which cause the acid to boil freely on applying heat, without danger of breaking the vessel. Arsenious acid, derived from arsenic in the sulphur used in the manufacture, has been lately detected in most of the oil of vitriol made in Germany; and from that source arsenic is introduced into preparations for which such acid is employed, as into phosphorus and hydrochloric acid. The arsenic is discovered by diluting with water and transmitting through the solution hydrosulphuric acid gas, which causes orpiment to be formed. The oil of vitriol may be purified from arsenious acid by adding a little hydrated peroxide of iron before distilling.

• *Prop.*—As obtained by the second process, pure sulphuric acid is a dense, colourless, oily fluid, which boils at 620° F., and has a sp. gr. in its most concentrated form, of 1.847 or a little higher, never exceeding 1.850. Mitscherlich found the density of its vapour to be 3; but the calculated number, 2.7617, is probably nearer the truth. It is one of the strongest acids with which chemists are acquainted, and when undiluted is powerfully corrosive. It decomposes all animal and vegetable substances by the aid of heat, causing deposition of charcoal and formation of water. It has a strong sour taste, and reddens litmus paper, even though greatly diluted. It unites with alkaline substances, and separates all other acids more or less completely from their combinations with the alkalis.

In a very concentrated state it dissolves small quantities of sulphur, and acquires a blue, green, or brown tint. Tellurium and selenium are also sparingly dissolved, the former causing a crimson, and the latter a green colour. By dilution with water, these substances subside unchanged; but if heat is applied, they are oxidized at the expense of the acid, and sulphurous acid gas is disengaged. Charcoal also appears soluble to a small extent in sulphuric acid, communicating at first a pink, and then a dark reddish brown tint.

It has a very great affinity for water, and unites with it in every proportion. The combination takes place with production of intense heat. When four parts by weight of the acid are suddenly mixed with one of water, the temperature of the mixture rises, according to Ure, to 300° . By its attraction for water it causes the sudden liquefaction of snow; and if mixed with it in due proportion (p. 60), intense cold is generated. It absorbs watery vapour with avidity from the air, and on this account is employed in the process for freezing water by its own evaporation. Its action in destroying the texture of the skin, and in decomposing animal and vegetable substances in general, seems dependent on its affinity for water.

To ascertain the quantity of real acid present in liquid acid of different strengths, dilute a known weight of the acid moderately with water, and, while warm, add pure anhydrous carbonate of soda, until the solution is exactly neutral. Every 58.3 parts of carbonate of soda, required to produce this effect, correspond to 40.1 parts of real sulphuric acid. If minute precision is not desired, the strength of the acid may be estimated by its sp. gr. according to the table of Ure inserted in the Appendix.

Sulphuric acid of commerce freezes at -15° . Diluted with water so as to have a sp. gr. of 1.78 it congeals even above 32° , and remains in the solid state, according to Keir, till the temperature rises to 45° . When mixed with rather more than its weight of water, its freezing point is lowered to -36° .

The composition of sulphuric acid as before given is founded on the observation of Gay-Lussac, that when the vapour of sulphuric acid is passed through a small porcelain tube heated to redness, it is resolved into two measures of sulphurous acid gas and one of oxygen. Berzelius has confirmed this conclusion by directly converting a known weight of sulphur into sulphuric acid.

Chemists possess an unerring test of the presence of sulphuric acid. If a solution of chloride of barium is added to a liquid containing sulphuric acid, it causes a white precipitate, sulphate of baryta, which is characterised by its insolubility in acids and alkalies.

Sulphuric acid does not occur free in nature, except occasionally in the neighbourhood of volcanoes. In combination, particularly with lime and baryta, it is very abundant.

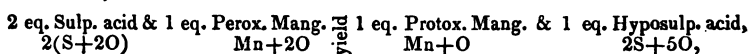
Hyposulphurous Acid.—It may be formed either by digesting sulphur in a solution of any sulphite, or by transmitting a current of sulphurous acid into a solution of sulphuret of calcium or strontium. In the former case, the sulphurous acid takes up an additional quantity of sulphur, and a salt of hyposulphurous acid is obtained; and in the latter, the sulphurous acid gives part of its oxygen to the metal, and its remaining oxygen unites with sulphur. Three equivalents of sulphurous acid and two of sulphuret of calcium contain the elements for forming two eq. of hyposulphite of lime, one eq. of sulphur being deposited. A convenient solution for this purpose is made by boiling 3 parts of slaked lime and one of sulphur with 20 parts of water for one hour, and decanting the clear liquid from the undissolved portions; but when this solution is used, the deposit of sulphur is abundant. Herschel states that hyposulphurous acid may be formed by the action of sulphurous acid on iron filings; but the nature of the change is not well understood.

The salts of hyposulphurous acid were first described by Gay-Lussac (An. de Ch. lxxxv.) under the name of *Sulphuretted Sulphites*. Thomson in his System of Chemistry suggested that the acid of these salts might be regarded as a compound of one equivalent of sulphur and one of oxygen, and proposed for it the name of

hyposulphurous acid; and the subsequent researches of Herschel (Phil. Journal, i. 8 and 396) accorded so entirely with this opinion, that it was universally adopted. But it appears from the experiments of Rose, that though the ratio of its elements is as 16 to 8, the equivalent of the acid, or the quantity required to neutralize 1 eq. of an alkali, is not 24, but 48; and hence that its smallest molecule must be formed of 2 atoms of sulphur united with 2 atoms of oxygen (Pog. Ann. xxi. 431).

Prop.—It cannot exist permanently in a free state. On decomposing a hyposulphite by any stronger acid, such as the sulphuric or hydrochloric, the hyposulphurous acid, at the moment of quitting the base, resolves itself into sulphurous acid and sulphur. Herschel succeeded in obtaining free hyposulphurous acid, by adding a slight excess of sulphuric acid to a dilute solution of hyposulphite of strontia; but its decomposition very soon took place, even at common temperatures, and was instantly effected by heat. Most of the hyposulphites are soluble in water, and have a bitter taste. The solution precipitates the nitrates of the oxides of silver and mercury black, as sulphuret of the metals; and salts of baryta and oxide of lead are thrown down as white insoluble hyposulphites of those bases. That of baryta is soluble without decomposition in water acidulated with hydrochloric acid. The solution of all the neutral hyposulphites has the peculiar property of dissolving recently precipitated chloride of silver in large quantity, and forming with it a liquid of an exceedingly sweet taste.

Hyposulphuric Acid.—It was discovered in 1819 by Welter and Gay-Lussac (An. de Ch. et Ph. x.), and is formed by transmitting a current of sulphurous acid gas through water containing peroxide of manganese in fine powder; when, by a new arrangement of their elements,



hyposulphate of protoxide of manganese remaining in solution. During the action heat is freely evolved, and in consequence sulphuric acid is also generated; but if the peroxide of manganese be pure and the materials kept cool, the formation of sulphuric acid is almost completely prevented. To the liquid, after filtration, a solution of pure baryta or sulphuret of barium in slight excess is added, whereby the manganese is thrown down as an oxide or sulphuret, sulphuric acid as sulphate of baryta, and a solution of hypo-

sulphate of baryta is obtained : the excess of baryta is got rid of by a free current of carbonic acid gas, and then heating the solution. The hyposulphate of baryta crystallizes by evaporation, and on decomposing a solution of that salt by a quantity of sulphuric acid exactly sufficient for precipitating the baryta, the hyposulphuric acid is left in solution.

Prop.—Taste sour ; distinct acid reaction ; neutralizes alkalies ; inodorous, and thus distinguished from sulphurous acid ; forms soluble salts with baryta, strontia, lime, and oxide of lead, by which it is distinguished from sulphuric acid. It cannot be obtained free from water. Its solution, if confined with a vessel of sulphuric acid under the exhausted receiver of an air pump, may be concentrated till it has a density of 1.347 ; but if an attempt is made to condense it still further, the acid is decomposed, sulphurous acid gas escapes, and sulphuric acid remains in solution. A similar change is still more readily produced if the evaporation is conducted by heat.

Welter and Gay-Lussac analyzed hyposulphuric acid by exposing neutral hyposulphate of baryta to heat. At a temperature a little above 212° this salt suffers complete decomposition ; sulphurous acid gas is disengaged, and neutral sulphate of baryta is obtained. It was thus ascertained that 72 grains of hyposulphuric acid yield 32 grains of sulphurous, and 40 of sulphuric acid ; from which it is inferred that hyposulphuric acid is composed either of an equivalent of each of those acids combined with each other, or of 2 eq. of sulphur and 5 of oxygen.

SECTION VIII.

PHOSPHORUS.

Hist. and Prep.—PHOSPHORUS (*φωσφόρος*, from *φῶς* light and *φέρειν* to carry), so called from its property of shining in the dark, was discovered about the year 1669 by Brandt, an alchemist of Hamburg. It was originally prepared from urine ; but Scheele, after Gahn's discovery of bones containing phosphate of lime, extracted it from that source. The bones are first ignited in an open fire till they become white, so as to destroy their animal matter, and burn away the charcoal derived from it, in which state they contain nearly 4-5ths of phosphate of lime. They are then reduced to a fine powder, and digested for a day or two with half their weight of strong sulphuric acid, with the addition of so much water

as will give the consistence of a thin paste. Decomposition of the phosphate of lime is thus effected, and two new salts formed, the sparingly soluble sulphate and a soluble superphosphate of lime. The latter is dissolved in warm water, and the solution, after being separated by filtration from the sulphate of lime, is evaporated to the consistence of syrup, mixed with a fourth of its weight of powdered charcoal, and strongly heated in an earthen retort well luted with clay. The beak of the retort is put into water, in which the phosphorus, as its vapour passes over, is condensed. When first obtained it is usually of a reddish brown colour, owing to the presence of phosphuret of carbon formed during the process. It may be purified by fusion in hot water, and being pressed while liquid through chamois leather, or by a second distillation.

In this process the oxygen of that part of the phosphoric acid which constitutes the superphosphate, unites with charcoal, giving rise to carbonic acid and carbonic oxide gases; and phosphate of lime in the state of bone earth, together with redundant charcoal, remains in the retort. The lime acts an important part in fixing the phosphoric acid, which if not so combined would distil over before the heat was high enough for its decomposition. In extracting phosphorus from urine, the phosphoric acid should be thrown down by acetate of the oxide of lead, and the insoluble salt converted by the action of sulphuric acid into the superphosphate, which is decomposed by charcoal as in the former process.

Prop.—When pure, transparent and almost colourless. At common temperatures it is a soft solid of sp. gr. 1.77; is easily cut with a knife, and the cut surface has a waxy lustre: at 108° it fuses, and at 550° is converted into vapour, which according to Dumas has a sp. gr. of 4.855. It is soluble by the aid of heat in naphtha, in fixed and volatile oils, in the chloride of sulphur, sulphuret of carbon, and sulphuret of phosphorus. On its cooling from solution in the latter, Mitscherlich obtained it in regular dodecahedral crystals. By the fusion and slow cooling of a large quantity of phosphorus, M. Frantween has obtained very fine crystals of an octohedral form, and as large as a cherry-stone. Thenard has remarked that when phosphorus is fused at 150°, and suddenly cooled by being plunged into cold water, it appears black; but by fusion and slow cooling it recovers its original aspect.

It is exceedingly inflammable. Exposed to the air at common temperatures, it undergoes slow combustion, emits a white vapour

of a peculiar alliaceous odour, appears distinctly luminous in the dark, and is gradually consumed. On this account, phosphorus should always be kept under water. The disappearance of oxygen which accompanies these changes is shown by putting a stick of phosphorus in a jar full of air, inverted over water. The volume of the gas gradually diminishes; and if the temperature of the air is at 60° , the whole of the oxygen will be withdrawn in the course of 12 or 24 hours. The residue is nitrogen gas, containing about 1-40th of its bulk of the vapour of phosphorus. It is remarkable that the slow combustion of phosphorus does not take place in pure oxygen, unless its temperature be about 80° . But if the oxygen be diluted with nitrogen, hydrogen, or carbonic acid gases, the oxidation occurs at 60° ; and it takes place at temperatures still lower in a vessel of pure oxygen, rarefied by diminished pressure. Mr. Graham finds that the presence of certain gaseous substances, even in minute quantity, has a remarkable effect in preventing the slow combustion of phosphorus: thus at 66° it is entirely prevented by the presence, (Quart. Jour. of Science, N. S. vi. 83.)

	Volumes of air.
of 1 volume of olefiant gas in . . .	450
1 ditto of vapour of sulphuric ether in . . .	150
1 ditto of vapour of naphtha in . . .	1820
1 ditto of vapour of oil of turpentine in . . .	4444,

and by an equally slight impregnation of the vapour of the other essential oils. Their influence is not confined to low temperatures.

Phosphorus becomes faintly luminous in the dark, in mixtures of

1 volume of air and 1 volume of olefiant gas at . . .	200° F.
1 . . . and 1 ditto of vapour of ether at . . .	215°
111 . . . and 1 ditto of vapour of naphtha at . . .	170°
156 . . . and 1 ditto of vapour of turpentine at . . .	186°.

It may be sublimed at its boiling temperature, in air containing a considerable proportion of the vapour of oil of turpentine, without diminishing the quantity of oxygen present, provided the heat be gradually and uniformly applied. Mr. Graham has also remarked, that the oxidation of phosphorus in the air is promoted by the presence of hydrochloric acid gas.

A very slight degree of heat is sufficient to inflame phosphorus in the open air. Gentle pressure between the fingers, friction, or a temperature not much above its point of fusion, kindles it readily. It burns rapidly even in the air, emitting a splendid white light, and causing intense heat. Its combustion is far more rapid in oxygen gas, and the light proportionally more vivid.

When phosphorus is kept for a long time under water, especially if exposed to light, its surface acquires a thin coating of white matter, which some have described as an oxide, and others as a hydrate of phosphorus. It seems according to Rose to be neither an oxide nor a hydrate, but phosphorus in a peculiar mechanical state, which deprives it of its usual action upon light and renders it opaque. (Pog. Annalen, xxvii. 565.)

Repeated researches by Berzelius have shown that the oxygen in phosphorous and phosphoric acids is in the ratio of 3 to 5, a result conformable to experiments on the same subject by Dulong, and admitted by most chemists. It is hence inferred that the smallest molecule of phosphoric acid contains 5 atoms of oxygen. Also Berzelius finds that 31.4 parts of phosphorus require 40 of oxygen for forming phosphoric acid: if this acid consist of one atom of phosphorus and five atoms of oxygen, 31.4 will represent one atom of phosphorus; or if the acid contain 2 atoms to 5, the atom of phosphorus will be half 31.4 or 15.7. It is doubtful which view is preferable, and I therefore continue to use the latter.

Its equivalent is therefore 15.7; eq. vol. = 25; symb. P.

The compounds of phosphorus described in this section are the following:—

	Phosp.	Oxygen.	Equiv.	Formulæ.
Oxide of Phosphorus	47.1 or 3 eq.	+ 8 or 1 eq.	= 55.1	3P+O or P ₃ O
Hypophosphorous acid	31.4 or 2 eq.	+ 8 or 1 eq.	= 39.4	2P+O or P ₂ O
Phosphorous acid	31.4 or 2 eq.	+ 24 or 3 eq.	= 55.4	2P+3O or P ₂ O ₃
Phosphoric acid	31.4 or 2 eq.	+ 40 or 5 eq.	= 71.4	2P+5O or P ₂ O ₅
Pyrophosphoric acid				
Metaphosphoric acid				

COMPOUNDS OF OXYGEN AND PHOSPHORUS.

Oxide.—When a jet of oxygen gas is thrown upon phosphorus while in fusion under hot water, combustion ensues, phosphoric acid is formed, and a number of red particles collect, which have been examined by M. Pelouze, who has shown them to be an oxide of phosphorus. The red matter left when phosphorus is burned, is probably of the same nature.

This, the only known oxide of phosphorus, is of a red colour, without taste or odour, and is insoluble in water, ether, alcohol, and oil. It is permanent in the air, even at 662° F., but takes fire at a low red heat. Heated to redness in a tube, phosphorus is expelled, and metaphosphoric acid remains. It takes fire in chlorine gas, and is rapidly oxidized by nitric acid. It does not

appear to possess any alkaline character. (An. de Ch. et Ph. l. 88.) Its equivalent is 55.1; symb. $3P + O$, or P_3O .

Hypophosphorous Acid.—This acid was discovered in 1816 by Dulong. (An. de Ch. et Ph. ii.) When water acts upon the phosphuret of barium the elements of both enter into a new arrangement, giving rise to phosphuretted hydrogen, phosphoric acid, hypophosphorous acid, and baryta. The former escapes in the form of gas, and the two latter combine with the baryta. Hypophosphite of baryta, being soluble, dissolves in the water, and may consequently be separated by filtration from the phosphate of baryta, which is insoluble. On adding a sufficient quantity of sulphuric acid for precipitating the baryta, hypophosphorous acid is obtained in a free state, and on evaporating the solution, a viscid liquid remains, highly acid and even crystallizable, which is a *hydrate of hypophosphorous acid*. When exposed to heat in close vessels, it undergoes the same kind of change as hydrated phosphorous acid.

Prop.—It is a powerful deoxidizing agent. It unites with alkaline bases; and it is remarkable that all its salts are soluble in water. The hypophosphites of potassa, soda, and ammonia, dissolve in every proportion in rectified alcohol; and hypophosphite of potassa is even more deliquescent than chloride of calcium. They are all decomposed by heat, and yield the same products as the acid itself. They are conveniently prepared by precipitating hypophosphite of baryta, strontia, or lime, with the alkaline carbonates; or by directly neutralizing these carbonates with hypophosphorous acid. The hypophosphite of baryta, strontia, and lime, are formed by boiling these earths in the caustic state in water together with fragments of phosphorus. The same change occurs as during the action of water on phosphuret of barium. The composition of this acid as stated at page 312, is on the authority of Rose. (Poggen. Annalen, ix. 367.) Its eq. is 39.4; symb. $2P + O$, \bar{P} , or P_2O .

Phosphorous Acid.—*Prep.*—When phosphorus is burned in air highly rarefied, imperfect oxidation ensues, and metaphosphoric and phosphorous acids are generated, the latter being obtained in the form of a white volatile powder. It may be procured more conveniently by subliming phosphorus through powdered bichloride of mercury contained in a glass tube; when a limpid liquid comes over, which is a compound of chlorine and phosphorus. (Davy's Elements, p. 288.) This substance and water mutually decompose each

other: the hydrogen of water unites with the chlorine, and forms hydrochloric acid; while the oxygen attaches itself to the phosphorus, and thus phosphorous acid is produced. The solution is then evaporated to the consistence of syrup to expel the hydrochloric acid; and the residue, which is hydrate of phosphorous acid, becomes a crystalline solid on cooling. It is also generated during the slow oxidation of phosphorus in atmospheric air. The product attracts moisture from the air, and forms an oil-like liquid. Dulong thinks that a distinct acid is produced in this case, which he calls *phosphatic acid*; but the opinion of Davy, that it is merely a mixture of phosphoric and phosphorous acids, is in my opinion perfectly correct.

Prop.—When obtained by the first process, it is anhydrous. Heated in the open air, it takes fire and forms metaphosphoric acid; but in close vessels it is resolved into metaphosphoric acid and phosphorus. The action of the hydrate under the latter circumstances is different, owing to the reaction of the elements of the water and acid, by which metaphosphoric acid and a gaseous compound of phosphorus and hydrogen are produced. The nature of this gas will be more particularly noticed in the section on phosphuretted hydrogen. It dissolves readily in water, has a sour taste, and smells somewhat like garlic. It unites with alkalis, and forms salts which are termed *phosphites*. The solution of phosphorous acid absorbs oxygen slowly from air, and is converted into phosphoric acid. From its tendency to unite with an additional quantity of oxygen, it is a powerful deoxidizing agent; and hence, like sulphurous acid, precipitates mercury, silver, platinum, and gold, from their saline combinations in the metallic form. Nitric acid converts it into phosphoric acid.

Its eq. is 55.4; symb. $2P + 3O$, \ddot{P} , or P_2O_3 .

Phosphoric Acid.—Hist.—It was shown in the year 1827 by Dr. Clarke, now Professor of Chemistry in Aberdeen, that under the term *phosphoric acid* had previously been confounded two distinct acids, one of which he proposed to distinguish by the name *pyrophosphoric acid* (from *πυρ* fire), to indicate that it is phosphoric acid modified by heat; and very lately Mr. Graham has described another modification of phosphoric acid, to which he has given the provisional name of metaphosphoric (from *μετα* together with), implying phosphoric acid and something besides; but this name is rather unfortunate, since it is applied to the only one of

the three modifications which can be obtained free from water. Perhaps paraphosphoric (from *παρά* near to) would be more appropriate. These three acids contain phosphorus and oxygen in the same ratio, and have the same equivalent, so that they may be considered as isomeric bodies (page 240); but that difference in the arrangement of their elements on which their peculiarities may be presumed to depend, is very slight, since they are easily convertible into each other. Mr. Graham, indeed, supposes the difference to arise solely from a disposition to unite in different proportions with water and alkaline bases; but this view scarcely suffices as an explanation, because it does not account for the peculiar disposition which causes their distinctive characters. (Phil. Trans. 1833, Part ii., and Phil. Mag. 3rd Series, iv. 401.)

Prep.—Phosphoric acid has hitherto been obtained only in combination with water or some alkaline base. One of the best modes for procuring it, is to oxidize phosphorus by strong nitric acid; but in this process care is necessary, as the action is sometimes very violent, and the escape of binoxide of nitrogen gas ungovernably rapid. It is safely conducted by adding fragments of phosphorus, or the so-called phosphatic acid, to strong nitric acid contained in a platinum crucible partially closed by its cover. Gentle heat is applied so as to commence, and, when necessary, to maintain moderate effervescence; and when one portion of phosphorus disappears, another is added, till the whole of the nitric acid is exhausted. The solution is then evaporated to dryness, and exposed to a red heat to expel the last traces of nitric acid. This should always be done in vessels of platinum, since phosphoric acid acts chemically upon those of glass or porcelain, and is thereby rendered impure. In this case, as in some other instances of the oxidation of combustibles by nitric acid, water is decomposed; and while its oxygen unites with phosphorus, its hydrogen combines with nitrogen of the nitric acid. A portion of ammonia, thus generated, is expelled by heat in the last part of the process.

Phosphoric acid may be prepared at a much cheaper rate from bones. For this purpose, superphosphate of lime, obtained in the way already described, should be boiled for a few minutes with excess of carbonate of ammonia. The lime is thus precipitated as a phosphate, and the solution contains phosphate, together with a little sulphate, of ammonia. The liquid, after filtration, is evaporated to dryness, and then ignited in a platinum crucible, by which means the ammonia and sulphuric acid are expelled.

In both the foregoing processes phosphoric acid exists only in solution; for on heating to redness in order to expel ammonia in the one case and nitric acid in the other, metaphosphoric acid is generated. To reproduce the phosphoric acid, the residue in the crucible requires to be dissolved in water and boiled for a few minutes.

Prop.—Phosphoric acid is colourless, intensely sour to the taste, reddens litmus strongly, and neutralizes alkalies; but it does not destroy the texture of the skin like sulphuric and nitric acids. Its solution may be evaporated at a temperature of 300° without decomposition, and when thus concentrated it assumes a dark colour, is as thick as treacle when cold, and consists of 71.4 parts or 1 eq. of phosphoric acid and 27 parts or 3 eq. of water. Mr. Graham obtained this hydrate in thin crystalline plates, which were extremely deliquescent, by keeping it for seven days *in vacuo* along with sulphuric acid. On heating this hydrate for several days to 415° , it lost nearly two-thirds of an equivalent of water, and then principally consisted of pyrophosphoric acid with two equivalents of water. At a still higher temperature metaphosphoric acid began to be formed; and at a red heat the conversion was complete. But after ignition it still contains water, amounting, according to Rose, to 9.44 per cent, which is rather more than an equivalent of water to one of metaphosphoric acid.

Phosphoric acid is remarkable for its tendency to unite with alkaline bases, in such proportions that the oxygen of the base and of the acid is as 3 to 5; or, in other words, it is prone to form subsalts, in which one equivalent of acid is combined with three equivalents of base. It manifests the same character in regard to water, and ceases to be phosphoric acid unless three equivalents of water to one of acid are present: it even appears that the water acts the part of a base, hence called *basic* water, and that the aqueous solution is not a mere solution of phosphoric acid, but of triphosphate of water, a sort of salt composed of one equivalent of acid and three equivalents of water. Part of this basic water enters along with soda into the constitution of two of the phosphates of soda, the water and soda together forming the three equivalents of base required by one equivalent of the acid. This point will be more fully described in the history of the phosphates.

When phosphoric acid is neutralized by ammonia and mixed with nitrate of oxide of silver, the yellow phosphate of that oxide subsides, a character by which it is distinguished from pyrophos-

phoric and metaphosphoric acids, as well as from all other acids except the arsenious. A certain test between phosphoric and arsenious acids is, that the former is neither changed in colour nor precipitated when a stream of hydrosulphate acid gas is transmitted through it; while the latter, with the required precautions, first acquires a yellow tint, and then yields a yellow precipitate.

Its eq. is 71.4; symb. $2P + 5O$, \underline{P}_5 , or PO_5 : but as it cannot exist uncombined, it is best denoted by $X_3. PO_5$, where X represents an equivalent of water or any base.

Pyrophosphoric Acid.—This acid is formed by exposing concentrated phosphoric acid for some time to a heat of 415° . Its general characters resemble phosphoric acid; but when neutralized by ammonia and mixed with nitrate of oxide of silver it yields a snow-white granular precipitate, pyrophosphate of that oxide, by which it is distinguished from phosphoric and metaphosphoric acids. In solution with cold water pyrophosphoric acid passes gradually, and at a boiling temperature rapidly, into phosphoric acid. Its salts, while neutral, are very permanent; but when boiled with either of the stronger acids in water, they are quickly converted more or less completely into phosphates.

Pyrophosphoric acid is remarkable for its tendency to unite with two equivalents of a base. Its aqueous solution probably contains a dipyrophosphate of water, that is, 1 eq. of the acid with 2 eq. of water, expressed by $2HO + P_2 O_5$, or $2HO. P_2 O_5$. This basic water is readily displaced by 2 eq. of stronger bases, such as soda; or if 1 eq. only of soda be added, then the soda and water together make up the 2 eq. of base, the formula of the salt being $NaO, HO. P_2 O_5$. The readiest mode of obtaining a pyrophosphate is to heat phosphoric acid with any fixed base in the ratio of one to two of their equivalents. This was done by Dr. Clarke in the experiments by which he established the existence of pyrophosphoric acid. (Brewster's Journal, vii. 298.) Phosphate of soda is a compound of 1 eq. phosphoric acid, 2 eq. soda, 1 eq. basic water, and 24 eq. water of crystallization, its formula being $2NaO, HO. P_2 O_5 + 24HO$: on drying this salt its water of crystallization is expelled, there remains $2NaO, HO. P_2 O_5$, which is still a phosphate, but on heating to redness the basic water is expelled, and $2Na. P_2 O_5$, pyrophosphate of soda, remains. By being forced to unite with 2 eq. of base, the acid acquires a disposition to do so on all occasions.

Its eq. is 71.4; symb. X_2 . $P_2 O_5$, X being used as above.

Metaphosphoric Acid.—This acid is obtained by burning phosphorus in dry air or oxygen gas, or heating to redness a concentrated solution of phosphoric or pyrophosphoric acids. By the former method the acid is a white solid, and anhydrous; in the latter it is a hydrate, or probably a metaphosphate of water, composed of 1 eq. acid and 1 eq. of water, its formula being $HO. P_2 O_5$. The water in this compound cannot be expelled by fire, since on attempting to do so by a violent heat, the whole is sublimed. In an open crucible it volatilizes at a temperature by no means high.

The peculiarity of this acid is to combine with one equivalent of a base. On exposing the anhydrous acid to the air it rapidly deliquesces, and at the same time acquires its basic water, which can only be replaced by an equivalent quantity of soda or some other alkaline base. The water is also driven off by fusion with siliceous or aluminous substances, with which the acid unites and forms very fusible compounds. The pure hydrated acid is of itself very fusible, and on cooling concretes into a transparent brittle solid, being known under the name of *glacial phosphoric acid*, which is highly deliquescent, and can hence only be preserved in its glassy state in bottles carefully closed.

The metaphosphoric resembles pyrophosphoric acid in the facility with which its aqueous solution passes into phosphoric acid. On the contrary, both of the other acids are converted into metaphosphates when heated to redness in contact with no more than one equivalent of certain fixed bases, such as potassa and soda. This acid when free occasions precipitation in solutions of the salts of baryta, and most of the earths and metallic oxides, and forms an insoluble compound with albumen. The metaphosphate of baryta and oxide of silver both fall in gelatinous flakes of a grey colour. Its eq. is 71.4; symb. $P_2 O_5$, or $X. P_2 O_5$.

SECTION IX.

BORON.

Hist. and Prep.—SIR H. DAVY discovered the existence of Boron in 1807 by exposing boracic acid to the action of a powerful galvanic battery; but he did not obtain a sufficient supply of

it for determining its properties. Gay-Lussac and Thenard * procured it in greater quantity in 1808 by heating boracic acid with potassium. The boracic acid is by this means deprived of its oxygen, and boron is set free. The easiest and most economical method of preparing this substance, according to Berzelius, is to decompose borofluoride of potassium or sodium by means of potassium. (*Annals of Philosophy*, xxvi. 128.)

Prop.—It is a dark olive-coloured substance, which has neither taste nor smell, and is a non-conductor of electricity. It is insoluble in water, alcohol, ether, and oils. It does not decompose water whether hot or cold. It bears intense heat in close vessels, without fusing or undergoing any other change except a slight increase of density. Its sp. gr. is about twice as great as that of water. It may be exposed to the atmosphere at common temperatures without change; but if heated to 600° , it suddenly takes fire, oxygen gas disappears, and boracic acid is generated. It is very difficult to oxidize all the boron by burning, because the boracic acid fuses at the moment of being formed, and by glazing the surface of the unburned boron protects it from oxidation. It also passes into boracic acid when heated with nitric acid, or with any substance that yields oxygen with facility.

According to the experiments of Davy and Berzelius, boron in burning unites with 68 per cent of oxygen; and the latter, from the composition of borax, estimates the oxygen in boracic acid at 68·8 per cent. In this, as in some other cases, where a combustible unites with oxygen in one proportion only, it is difficult with any certainty to assign the true atomic constitution of the compound. Boracic acid may be a compound of boron and oxygen in the ratio of 1 atom to 1 atom, in that of 1 to 2 as supposed by Thomson, or of 1 to 3. When dry boracic acid is heated with charcoal in chlorine gas, it is decomposed, and two volumes of chloride of boron and three of carbonic oxide gas are produced. The latter contains $1\frac{1}{2}$ volumes of oxygen, and the former has been proved by Dumas to be composed of 3 volumes of chlorine united with 1 volume of the vapour of boron, the density of which is estimated at ·751, its eq. vol. being 100. From this it may be deduced that the constitution of boracic acid is BO_3 , which has also been recently adopted by Berzelius (*Pog. An.* xxiv. 561). Hence its eq. is 10·9; eq. vol. = 100; symb. B.

* *Recherches Physico-Chimiques*, vol. i.

Boric Acid.—*Hist. and Prep.*—This is the only known compound of boron and oxygen. As a natural product it is found in the hot springs of Lipari, and in those of Sasso in the Florentine territory. It is a constituent of several minerals, among which the datolite and boracite may in particular be mentioned. It occurs much more abundantly under the form of borax, a native compound of boric acid and soda. It is prepared for chemical purposes by adding sulphuric acid to a solution of purified borax in about four times its weight of boiling water, till the liquid acquires a distinct acid reaction. The sulphuric acid unites with the soda; and the boric acid is deposited, when the solution cools, in a confused group of shining scaly crystals. It is then thrown on a filter, washed with cold water to separate the adhering sulphate of soda and sulphuric acid, and still further purified by solution in boiling water and re-crystallization. But even after this treatment it is apt to retain a little sulphuric acid; on this account, when required to be absolutely pure, it should be fused in a platinum crucible, and once more dissolved in hot water and crystallized.

Prop.—In the crystallized state it is a hydrate, which contains 43.62 per cent of water, being a ratio of 34.9 parts or 1 eq. of the anhydrous acid to 27 parts or 3 eq. of water. This hydrate dissolves in 25.7 times its weight of water at 60°, and in 3 times at 212°. Boiling alcohol dissolves it freely, and the solution, when set on fire, burns with a beautiful green flame; a test which affords the surest indication of the presence of boric acid. Its sp. gr. is 1.479. It has no odour, and its taste is rather bitter than acid. It reddens litmus paper feebly, and effervesces with alkaline carbonates. Faraday has noticed that it renders turmeric paper brown like the alkalis. From the weakness of the acid properties of boric acid, all the borates, when in solution, are decomposed by the stronger acids; and the neutral borates of potash and soda are deprived of half their base by carbonic acid, at common temperatures.

When hydrous boric acid is exposed to a gradually increasing heat in a platinum crucible, its water of crystallization is wholly expelled, and a fused mass remains which bears a white heat without being sublimed. On cooling, it forms a hard, colourless, transparent glass, which is anhydrous boric acid. If the water of crystallization be driven off by the sudden application of a strong heat, a large quantity of boric acid is carried away during the rapid escape of watery vapour. The same happens, though in a less

degree, when a solution of boracic acid in water is boiled briskly. Vitrified boracic acid should be preserved in well-stopped vessels; for if exposed to the air, it absorbs water, and gradually loses its transparency. Its sp. gravity is 1.803. It is exceedingly fusible, and communicates this property to the substances with which it unites. For this reason borax is often used as a flux.

Its eq. is 84.9; symb. $B + 3O$, \ddot{B} , or BO_3 .

SECTION X.

SILICON.

Hist.—THAT silicic acid or silica is composed of a combustible body united with oxygen, was demonstrated by Davy; for on bringing the vapour of potassium in contact with pure silicic acid heated to whiteness, a silicate of potassa resulted, through which was diffused the inflammable base of silicic acid in the form of black particles like plumbago. To this substance, on the supposition of its being a metal, the term *silicium* was applied. But though this view has been adopted by most chemists, so little was known with certainty concerning the real nature of the base of silica, that Thomson inclined to the opinion of its being a non-metallic body, and accordingly associated it in his system of chemistry with carbon and boron under the name of *silicon*. The recent researches of Berzelius appear almost decisive of this question. A substance which wants the metallic lustre, and is a non-conductor of electricity, cannot be regarded as a metal.

Prep.—Pure silicon was first procured by Berzelius in the year 1824 by the action of potassium on fluosilicic acid gas, but it is more conveniently prepared from the double fluoride of silicon and potassium or sodium, previously dried by a temperature near that of redness. When this compound is heated in a glass tube with potassium, the latter unites with fluorine, and silicon is separated. The heat of a spirit-lamp is sufficient for the purpose, and the decomposition takes place, accompanied with feeble detonation, before the mixture becomes red hot. When the mass is cold, the soluble parts are removed by the action of water; the first portions of which produce disengagement of hydrogen gas, owing to the presence of some silicuret of potassium. The silicon thus procured is chemically united with a little hydrogen, and at a red heat burns vividly

in oxygen gas. In order to render it quite pure, it should be first heated to redness, and then digested in dilute hydrofluoric acid to dissolve adherent particles of silicic acid. (Ann. of Phil. xxvi. 116.)

Prop.—Silicon obtained in this manner has a dark nut-brown colour, without the least trace of metallic lustre. It is a non-conductor of electricity. It is incombustible in air and in oxygen gas; and may be exposed to the flame of the blowpipe without fusing or undergoing any other change. It is neither dissolved nor oxidized by the sulphuric, nitric, hydrochloric, or hydrofluoric acids; but a mixture of the nitric and hydrofluoric acids dissolves it readily even in the cold.

It is not changed by ignition with chlorate of potassa. In nitre it does not deflagrate until the temperature is raised so high that the acid is decomposed; and then the oxidation is effected by the affinity of the disengaged alkali for silicic acid co-operating with the attraction of oxygen for silicon. For a similar reason it burns vividly when brought into contact with carbonate of potassa or soda, and the combustion ensues at a temperature considerably below that of redness. It explodes in consequence of a copious evolution of hydrogen gas, when it is dropped upon the fused hydrate of potassa, soda, or baryta.

Berzelius ascertained, by oxidizing a known weight of silicon, that 100 parts of silicic acid are composed of 48.4 of silicon and 51.6 of oxygen. Now, if silicic acid, as Thomson supposes, be composed of single atoms of its elements, then the equivalent of silicon will be 7.5; but if, as Berzelius believes, the smallest molecule of that acid contain 3 atoms of oxygen united with 1 atom of silicium, the equivalent of silicium would be 22.5. The latter view is supported by very strong analogies. Its equivalent is therefore 22.5; symb. Si.

Silicic Acid.—*Hist. and Prep.*—This compound, known also by the names of *silica* and *siliceous earth*, exists abundantly in nature. It enters into the composition of most of the earthy minerals; and under the name of quartz rock, forms independent mountainous masses. It is the chief ingredient of sandstones, flint, calcedony, rock crystal, and other analogous substances. It may indeed be procured, of sufficient purity for most purposes, by igniting transparent specimens of rock crystal, throwing them while red-hot into water, and then reducing them to powder.

Prop.—Pure silicic acid, in this state, is a light white powder,

which feels rough and dry when rubbed between the fingers ; is both insipid and inodorous ; the sp. gr. is 2.69. It is fixed in the fire, and very infusible ; but fuses before the oxy-hydrogen blowpipe with greater facility than lime or magnesia. It is quite insoluble in water ; but Berzelius has shown, that if presented to water while in the nascent state, it is dissolved in large quantity. On evaporating the solution gently, a bulky gelatinous hydrate separates, which is partially decomposed by a very moderate temperature, but does not part with all its water except at a red heat.

Silicic acid has no action on test paper ; but in all its chemical relations it manifests the properties of an acid, and displaces carbonic acid by the aid of heat from the alkalies. Its combinations with the fixed alkalies are effected by mixing pure sand with carbonate of potassa or soda, and heating the mixture to redness. During the process, carbonic acid is expelled, and a silicate of the alkali is generated. The nature of the product depends upon the proportions which are employed. On igniting one part of silicic acid with three of carbonate of potassa, a vitreous mass is formed, which is deliquescent, and may be dissolved completely in water. This solution, which was formerly called *liquor silicum*, has an alkaline reaction, and absorbs carbonic acid on exposure to the atmosphere, by which it is partially decomposed. Concentrated acids precipitate the silicic acid as a gelatinous hydrate ; but if a considerable quantity of water is present, and the acid is added gradually, the alkali may be perfectly neutralized without any separation of silicic acid. When a solution of this kind is evaporated to dryness, the silicic acid is rendered quite insoluble, and may thus be obtained in a pure form.

But if the proportion of silicic acid and alkali be reversed, a transparent brittle compound results, which is insoluble in water, is attacked by none of the acids excepting the hydrofluoric, and possesses the well-known properties of glass. Every kind of ordinary glass is a silicate, and all its varieties are owing to differences in the proportion of the constituents, to the nature of the alkali, or to the presence of foreign matters. Thus, green bottle glass is made of impure materials, such as river sand, which contains iron, and the most common kind of kelp or pearl-ashes. Crown glass for windows is made of a purer alkali, and sand which is free from iron. Plate glass, for looking-glasses, is composed of sand and alkali in their purest state ; and in the formation of flint-glass, besides these pure

ingredients, a considerable quantity of litharge or red lead is employed. A small portion of peroxide of manganese is also used, in order to oxidize carbonaceous matters contained in the materials of the glass; and nitre is sometimes added with the same intention. Ordinary flint-glass, according to Faraday, contains 51.93 per cent of silicic acid, 33.28 of oxide of lead, and 13.77 of potassa; proportions which correspond to 1 eq. of potassa, 1 eq. of oxide of lead, and nearly 4 eq. of silicic acid. Flint-glass, accordingly, is a double salt, consisting chiefly of bisilicate of potassa and bisilicate of oxide of lead.

Its eq. is 46.5; symb. Si + 3O, $\ddot{\text{Si}}$, or SO_3 .

SECTION XI.

SELENIUM.

Hist. and Prep.—This substance was discovered in 1818 by Berzelius, who called it selenium, from $\Sigma\epsilon\lambda\eta\eta$, the *Moon*, suggested by its having at first been mistaken for the metal tellurium. (An. de Ch. et Ph. ix. 160, and An. of Phil. xiii. 401.) It has hitherto been obtained in very small quantity, and occurs for the most part in combination with some varieties of iron pyrites. Stromeyer has also detected it, as a sulphuret of selenium, among the volcanic products of the Lipari isles. It is found likewise at Clausthal in the Hartz, combined, according to Stromeyer and Rose, with several metals, such as lead, cobalt, silver, mercury, and copper. Berzelius found it in the sulphur obtained by sublimation from the iron pyrites of Fahlun. In a manufactory of sulphuric acid, at which this sulphur was employed, it was observed that a reddish-coloured matter always collected at the bottom of the leaden chamber; and on burning this substance, Berzelius perceived a strong and peculiar odour, similar to that of decayed horse-radish, which induced him to submit it to a careful examination, and thus led to the discovery of selenium. For the extraction of selenium from the native sulphuret, Magnus proposes to mix it with eight times its weight of peroxide of manganese, and to expose the mixture to a low red heat in a glass retort, the beak of which dips into water. The sulphur, oxidized at the expense of the manganese, escapes in the form of sulphurous acid; while the selenium either sublimes as such or in the state of selenious acid. Should any of the latter be carried over into the water, it would there be reduced by the sulphurous acid.

Prop.—Selenium, at common temperatures, is a brittle opaque solid body, without taste or odour. It has a metallic lustre and the aspect of lead, when in mass; but it is of a deep red colour when reduced to powder. Its sp. gr. is between 4.3 and 4.32. At 212° it softens, and is then so tenacious that it may be drawn out into fine threads which are transparent, and appear red by transmitted light. It becomes quite fluid at a temperature somewhat above that of boiling water. It boils at about 650°, forming a vapour which has a deep yellow colour, but is free from odour. It may be sublimed in close vessels without change, and condenses again into dark globules of a metallic lustre, or as a cinnabar red powder, according as the space in which it collects is small or large. Berzelius at first regarded it as a metal; but, since it is an imperfect conductor of heat and electricity, it more properly belongs to the class of the simple non-metallic bodies.

Selenium is insoluble in water. It suffers no change from mere exposure to the atmosphere; but if heated in the open air, it combines readily with oxygen, and two compounds, oxide of selenium and selenious acid, are generated. If exposed to the oxidizing part of the blow-pipe flame, it tinges the flame with a light blue colour, and exhales so strong an odour of decayed horse-radish, that 1-50th of a grain is said to be sufficient to scent the air of a large apartment. By this character the presence of selenium, whether alone or in combination, may always be detected.

Berzelius has shown that selenic acid is composed of 24 parts of oxygen and 39.6 of selenium. This substance, also, has three grades of oxidation, the oxygen in the two last of which is in the ratio of 2 and 3; and the highest grade, selenic acid, has in all its chemical relations a singularly close analogy to sulphuric acid. From these facts it is inferred that selenic acid is composed of 1 atom of selenium and 3 atoms of oxygen. Its eq. is 39.6; symb. Se.

The compounds of selenium described in this section are the following:—

	Selenium.	Oxygen.	Equiv. Formulæ.
Oxide of Selenium (probably)	39.6 or 1 eq. +	8 or 1 eq. =	47.6 Se+O.
Selenious Acid	39.6	+ 16 or 2 eq. =	55.6 Se+2O.
Selenic Acid	39.6	+ 24 or 3 eq. =	63.6 Se+3O.

Oxide of Selenium.—This compound is formed in greatest abundance by heating selenium in a limited quantity of atmospheric air, and by washing the product to separate selenious acid, which is generated at the same time. It is a colourless gas, which

is very sparingly soluble in water, and does not possess any acid properties. It is the cause of the peculiar odour which is emitted during the oxidation of selenium.

Selenious Acid.—This acid is most conveniently prepared by digesting selenium in nitric or nitro-hydrochloric acid till it is completely dissolved. On evaporating the solution to dryness, a white residue is left, which is selenious acid. By increase of temperature, the acid itself sublimes, and condenses again unchanged into long four-sided needles. It attracts moisture from the air, whereby it suffers imperfect liquefaction. It dissolves in alcohol and water. It has distinct acid properties, and its salts are called *selenites*.

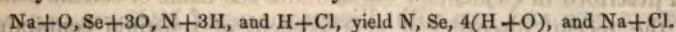
Selenious acid is readily decomposed by all substances which have a strong affinity for oxygen, such as sulphurous and phosphorous acids. When sulphurous acid, or an alkaline sulphite, is added to a solution of selenious acid, a red-coloured powder, pure selenium, is thrown down, and the sulphurous is converted into sulphuric acid. Hydrosulphuric acid also decomposes it; and an orange-yellow precipitate subsides, which is a sulphuret of selenium.

Selenic Acid.—*Hist.*—The preceding compound, discovered by Berzelius, was till lately the only known acid of selenium, and has been described in elementary works under the name of selenic acid; but the recent discovery of another acid of selenium containing more oxygen than the other, has rendered necessary a change of nomenclature. The existence of selenic acid was first noticed by M. Nitzsch, assistant of Mitscherlich, and its properties have been examined and described by the Professor himself. (*Edin. Journal of Science*, viii. 294.)

Prep.—This acid is prepared by fusing nitrate of potassa or soda with selenium, a metallic seleniuret, or with selenious acid or any of its salts. Seleniuret of lead, as the most common ore of selenium, will generally be employed; but it is very difficult to obtain pure selenic acid by its means, because it is commonly associated with metallic sulphurets. The ore is first treated with hydrochloric acid to remove any carbonate that may be present; and the insoluble part, which is about a third of the mass, is mixed with its own weight of nitrate of soda, and thrown by successive portions into a red-hot crucible. The lead is thus oxidized, and the selenium converted into selenic acid, which unites with soda. The fused mass is then acted on by hot water, which dissolves only seleniate of soda, together with nitrate and nitrite of soda; while

the insoluble matter, when well washed, is quite free from selenium. The solution is next made to boil briskly, when anhydrous seleniate of soda is deposited; while, on cooling, nitrate of soda crystallizes. On renewing the ebullition and subsequent cooling, fresh portions of seleniate and nitrate are procured; and these successive operations are repeated, until the former salt is entirely separated. This process is founded on the fact, that seleniate of soda, like the sulphate of the same base, is more soluble in water of about 90° than at higher or lower temperatures. The nitrite of soda, formed during the fusion, is purposely reconverted into nitrate by digestion with nitric acid.

The seleniate of soda thus procured always contains a little sulphuric acid, derived from the metallic sulphurets of the ore; and it is not possible to separate this acid by crystallization. All attempts to separate it by means of baryta were likewise fruitless; and the only method of effecting this object is by reducing the selenic acid into selenium. This is done by heating a mixture of seleniate of soda with hydrochlorate of ammonia, when the sodium unites with chlorine, all the hydrogen with oxygen, and selenium and nitrogen are set free. This change will be more readily followed when stated in symbols;—thus



The selenium which sublimes is quite free from sulphur. It is then converted by nitric acid into selenious acid, which should be neutralized with soda, and fused with nitre or nitrate of soda. The pure seleniate of soda, separated from the nitrate according to the foregoing process, is subsequently dissolved in water, and obtained in crystals by spontaneous evaporation.

To procure the acid in a free state, seleniate of soda is decomposed by nitrate of oxide of lead. The seleniate of that oxide, which is as insoluble as the sulphate, after being well washed, is exposed to a current of hydrosulphuric acid gas, which precipitates all the lead as a sulphuret, but does not decompose the selenic acid. The excess of the gas is driven off by heat, and pure selenic acid remains diluted with water. The absence of fixed substances may be proved by its being volatilized by heat without residue; and if free from sulphuric acid, it gives no precipitate with chloride of barium after being boiled with hydrochloric acid. Any nitric acid which may be present is expelled by concentrating the solution by means of heat.

Prop.—It is a colourless liquid, which may be heated to 536° , without appreciable decomposition; but above that point decomposition commences, and it becomes rapid at 554° , giving rise to disengagement of oxygen and selenious acid. When concentrated by a temperature of 329° , its sp. gr. is 2.524; at 512° it is 2.60, and at 545° it is 2.625, but a little selenious acid is then present. When procured by the process above described, selenic acid always contains water, but it is very difficult to ascertain its precise proportion. Some acid, which had been heated higher than 536° , contained, subtracting the quantity of selenious acid present, 15.75 per cent of water, which approximates to the ratio of one equivalent of water and one of the acid. It is certain that selenic acid is decomposed by heat before parting with all the water which it contains.

Selenic acid has a powerful affinity for water, and emits as much heat in uniting with it as sulphuric acid does. Like this acid it is not decomposed by hydrosulphuric acid, and hence this gas may be employed for decomposing seleniate of the oxides of lead or copper. With hydrochloric acid the change is peculiar; for on boiling the mixture mutual decomposition ensues, water and selenious acid are formed, and chlorine is set free; so that the solution, like *aqua regia*, is capable of dissolving gold and platinum. Selenic acid dissolves zinc and iron with disengagement of hydrogen gas, and copper with formation of selenious acid. It dissolves gold also, but not platinum. Sulphurous acid has no action on selenic acid, whereas selenious acid is easily reduced by it. Consequently, when it is wished to precipitate selenium from selenic acid, it must be boiled with hydrochloric acid before sulphurous acid is added.

Mitscherlich has observed, that selenic and sulphuric acids are not only analogous in composition and in many of their properties, but that the similarity runs through their compounds with alkaline substances, their salts resembling each other in chemical properties, constitution, and form.

SECTION XII.

CHLORINE.

Hist.—THE discovery of chlorine was made in the year 1774 by Scheele, while investigating the nature of manganese, and he described it under the name of *dephlogisticated marine acid*. The French chemists called it *oxygenized muriatic acid*, a term which

was afterwards contracted to *oxy-muriatic acid*, from an opinion proposed by Berthollet that it is a compound of *muriatic acid* and *oxygen*. In 1809 Gay-Lussac and Thénard published an abstract of some experiments upon this substance, which subsequently appeared at length in their *Recherches Physico-Chimiques*, wherein they stated that oxy-muriatic acid might be regarded as a simple body, though they gave the preference to the doctrine advanced by Berthollet. Davy engaged in the inquiry about the same time; and after having exposed oxy-muriatic acid to the most powerful decomposing agents which chemists possess, without being able to effect its decomposition, he communicated to the Royal Society an essay, in which he denied its compound nature; and he maintained that, according to the true logic of chemistry, it is entitled to rank with simple bodies. This view, which is commonly termed the *new theory of chlorine*, though strongly objected to at the time it was first proposed, is now universally received by chemists. The grounds of preference will hereafter be briefly stated.

Prep.—Chlorine gas is obtained by the action of hydrochloric acid on peroxide of manganese. The most convenient method of preparing it is by mixing concentrated hydrochloric acid, contained in a glass flask, with half its weight of finely powdered peroxide of manganese. Effervescence, owing to the escape of chlorine, takes place even in the cold; but the gas is evolved much more freely by the application of a moderate heat. It should be collected in inverted glass bottles filled with warm water; and when the water is wholly displaced by the gas, the bottles should be closed with a well-ground glass stopper. As some hydrochloric acid gas commonly passes over with it, the chlorine should not be considered quite pure, till after being transmitted through water.

The theory of this process will be readily understood by first viewing the elements which act on each other, namely,—

Manganese .	27.7 or 1 eq.	Mn	Chlorine .	70.84 or 2 eq.	2Cl
Oxygen .	16	2 eq. 2 O	Hydrogen .	or 2 eq.	2H
Perox. of Mang.	43.7 or 1 eq.	Mn+2O	Hydrochl. acid	72.84 or 2 eq. 2(H+Cl);	

and then inspecting the products derived from them, namely,

Manganese . .	27.7	Hydrogen	2	Chlorine	35.42 or 1 eq.
Chlorine . . .	35.42	Oxygen	16		
Chloride of Mang.	63.12	Water	18		

In symbols, $Mn+2O$, and $2(H+Cl)$, yield $Mn+Cl$, $2(H+O)$, and Cl .

The affinities which determine these changes are the mutual attraction of oxygen and hydrogen, and of chlorine and manganese.

When it is an object to prepare chlorine at the cheapest rate, as for the purposes of manufacture, the preceding process is modified in the following manner. Three parts of sea-salt are intimately mixed with one of peroxide of manganese, and to this mixture two parts of sulphuric acid, diluted with an equal weight of water, are added. By the action of sulphuric acid on sea-salt, hydrochloric acid is disengaged, which reacts as in the former case upon the peroxide of manganese; so that, instead of adding hydrochloric acid directly to the manganese, the materials for forming it are employed. In this process, however, the sulphates of soda and protoxide of manganese are generated, instead of chloride of manganese. Thus the materials which act on each other are MnO_2 , NaCl , and 2SO_3 ; and the products MnO , SO_3 , NaO , SO_3 , and Cl .

Prop.—Chlorine (from *χλωρος*, green) is a yellowish-green coloured gas, which has an astringent taste, and a disagreeable odour. It is one of the most suffocating of the gases, exciting spasm and great irritation of the glottis, even when considerably diluted with air. When strongly and suddenly compressed, it emits both heat and light, the latter being solely due, as in the case of air and oxygen, to the chlorine acting chemically on the oil with which the compressing apparatus is lubricated (*An. de Ch. et Ph.* xliv. 181). According to Davy 100 cubic inches of dry chlorine, at 30 B. and 60 F. weigh between 76 and 77 grains. Gay-Lussac and Thenard found the density of pure and dry chlorine to be 2.47, which gives 76.599 grains as the weight of 100 cubic inches at 60° F. and 30° B. Under the pressure of about four atmospheres it is a limpid liquid of a bright yellow colour, which does not freeze at the temperature of zero, and which assumes the gaseous form with the appearance of ebullition when the pressure is removed. Kemp finds that this liquid is a non-conductor of electricity.

Cold recently boiled water, at the common pressure, absorbs twice its volume of chlorine, and yields it again when heated. The solution, which is made by transmitting a current of chlorine gas through cold water, has the colour, taste, and most of the other properties of the gas itself. When moist chlorine gas is exposed to a cold of 32°, yellow crystals are formed, which consist of water and chlorine in definite proportions. They are composed, accord-

ing to Faraday, of 35.42 parts or 1 eq. of chlorine, and 90 parts or 10 eq. of water. It experiences no chemical change from the action of the imponderables. Thus it is not affected chemically by intense heat, by strong shocks of electricity, or by a powerful galvanic battery. Davy exposed it also to the action of charcoal heated to whiteness by galvanic electricity, without separating oxygen from it, or in any way affecting its nature. Light does not act on dry chlorine; but if water be present, the chlorine decomposes that liquid, unites with the hydrogen to form hydrochloric acid, and oxygen gas is set at liberty. This change takes place quickly in sunshine, more slowly in diffused daylight, and not at all when light is wholly excluded. Hence the necessity of keeping moist chlorine gas, or its solution, in a dark place.

Chlorine unites with some substances with evolution of heat and light, and is hence termed a supporter of combustion. On plunging a lighted taper into chlorine gas, it burns for a short time with a small red flame, and emits a large quantity of smoke. Phosphorus takes fire in it spontaneously, and burns with a pale white light. Several of the metals, such as tin, copper, arsenic, antimony, and zinc, when introduced into chlorine in the state of powder or in fine leaves, are suddenly inflamed. In all these cases the combustible substances unite with chlorine.

Chlorine has a very powerful attraction for hydrogen; and many of the chemical phenomena, to which it gives rise, are owing to this property. A striking example is its power of decomposing water by the action of light, or at a red heat; the same effect is produced on most compound substances, of which hydrogen is an element. For the same reason, when chlorine, water, and some other body which has a strong affinity for oxygen, are presented to one another, water is usually resolved into its elements, its hydrogen attaching itself to the chlorine, and its oxygen to the other body. Thus chlorine is, indirectly, one of the most powerful oxidizing agents which we possess.

When any compound of chlorine and an inflammable is exposed to the influence of galvanism, the inflammable body goes over to the —, and chlorine to the + pole of the battery. This establishes a close analogy between oxygen and chlorine, both of them being supporters of combustion, and both negative electrics.

Though formerly called an acid, it possesses no acid properties. It has not a sour taste, does not redden the blue colour of plants,

and shows comparatively little disposition to unite with alkalis. Its strong affinity for the metals is sufficient to prove that it is not an acid; for chemists are not acquainted with any instance of an acid combining directly in definite proportion with a metal. Its action on the pure alkalis leads to complicated changes, which will be considered while speaking of the oxides of chlorine.

One of the most important properties of chlorine is its bleaching power. All animal and vegetable colours are speedily removed by chlorine; and when the colour is once discharged, it can never be restored. Davy proved that chlorine cannot bleach unless water is present. Thus dry litmus paper suffers no change in dry chlorine; but when water is admitted, the colour speedily disappears. It is well known also that hydrochloric acid is always generated when chlorine bleaches. From these facts it is inferred that water is decomposed during the process; that its hydrogen unites with chlorine, and that decomposition of the colouring matter is occasioned by the oxygen which is liberated. The bleaching property of binoxide of hydrogen and of chromic and permanganic acids, of which oxygen is certainly the decolorizing principle, leaves little doubt of the accuracy of the foregoing explanation.

Chlorine is useful, likewise, for the purposes of fumigation. The experience of Guyton-Morveau is sufficient evidence of its power in destroying the volatile principles given off by putrefying animal matter; it probably acts in a similar way on contagious effluvia. A peculiar compound, formed by the action of chlorine on soda, has been lately introduced for this purpose by Labarraque.

Chlorine is in general easily recognised by its colour and odour. Chemically it may be detected by its bleaching property, added to the circumstance that a solution of nitrate of oxide of silver occasions in it a dense white precipitate (a compound of chlorine and metallic silver), which becomes dark on exposure to light, is insoluble in acids, and dissolves completely in pure ammonia. The whole of the chlorine, however, is not thrown down; for the oxygen of the oxide of silver unites with a portion of chlorine, and converts it into chloric acid.

Those compounds of chlorine, which are not acid, are termed *chlorides* or *chlorurets*. The former expression, from the analogy between chlorine and oxygen, is perhaps the more appropriate.

Berzelius inferred the equivalent of chlorine from the oxygen lost

by chlorate of potassa when decomposed by heat, and the quantity of chlorine found in the residual chloride of potassium. I investigated the same subject by examining into the composition of the nitrate, of the oxide and chloride of silver, of the protoxide and chloride of lead, and of the peroxide and chlorides of mercury. These researches concur in showing 36, the eq. of chlorine commonly adopted in this country, to be erroneous. The number inferred from the sp. gr. of chlorine and hydrogen gases is 35.84 (page 131); but, unfortunately, the densities of these gases are not known with the precision required for an application of this nature.

Its eq. is 35.42; eq. vol. = 100; symb. Cl.

The composition of the compounds described in this section is as follows:—

Chlorine.			Equiv.	Formulæ.
Hydrochloric Acid	35.42	1 eq. + Hydrogen	1 1 eq. = 36.42	H + Cl
Hypochlorous Acid	35.42	+ Oxygen	8 1 eq. = 43.42	Cl + O
Chlorous Acid	35.42	+ Ditto	16 2 eq. = 51.42	Cl + 2O
Chloric Acid	35.42	+ Ditto	40 5 eq. = 75.42	Cl + 5O
Perchloric Acid	35.42	+ Ditto	56 7 eq. = 91.42	Cl + 7O
Quadrochloride of Nitrogen	141.68	4 eq. + Nitrogen	14.15 1 eq. = 155.83	N + 4Cl
Protochloride of Carbon	35.42	1 eq. + Carbon	6.12 1 eq. = 41.54	C + Cl
Dichloride of Carbon	35.42	1 eq. + Ditto	12.24 2 eq. = 47.66	2C + Cl
Perchloride of Carbon	106.26	3 eq. + Carbon	12.24 2 eq. = 118.50	2C + 3Cl
Dichloride of Sulphur	35.42	1 eq. + Sulphur	32.2 2 eq. = 67.62	S + Cl
Bichloride of Sulphur	70	2 eq. + Ditto	16.1 1 eq. = 86.1	S + 2Cl
Sesquichloride of Phosphorus	106.26	3 eq. + Phospho.	31.4 1 eq. = 137.66	2P + 3Cl
Perchloride of Phosphorus	175	5 eq. + Ditto	31.4 1 eq. = 206.4	2P + 4Cl
Chlorocarbonic acid gas	35.42	1 eq. + Carb. ox.	14.12 1 eq. = 49.54	CO + Cl
Terchloride of Boron	106.26	3 eq. + Boron	10.9 1 eq. = 117.16	B + 3Cl
Terchloride of Silicon	106.26	3 eq. + Silicon	22.5 1 eq. = 128.76	Si + 3Cl

Hydrochloric Acid.—Hist. and Prep.—A concentrated aqueous solution of this acid has been long known under the names of spirit of salt, and of marine or muriatic acid; but in its purer form of gas it was discovered in 1772 by Priestley. It may be conveniently

prepared by putting an ounce of strong hydrochloric acid solution into a glass flask, and heating it by means of a lamp till the liquid boils, when the gas is freely evolved, and may be collected over mercury. Another method of preparing it is by the action of concentrated sulphuric acid on an equal weight of sea-salt. Brisk effervescence ensues at the moment of making the mixture, and on the application of heat a large quantity of hydrochloric acid gas is disengaged. In the former process, hydrochloric acid previously dissolved in water is simply expelled from the solution by heat. The explanation of the latter process is more complicated. Sea-salt was formerly supposed to be a compound of hydrochloric acid and soda; and, on this supposition, the soda was believed merely to quit the hydrochloric and unite with sulphuric acid. But the researches of Gay-Lussac, Thenard, and Davy, proved that it consists of chlorine and sodium combined in the ratio of their equivalents. The nature of its action with sulphuric acid will be understood by comparing the elements concerned in the change before and after it has occurred:—

Hydrous Sulp. Acid.	Chloride of Sodium.	Sulp. of Soda.	Hydrochloric Acid.
Real Acid 40·1	Chlorine 35·42	Acid 40·1	Chlorine 35·42
Water { Hyd. 1 } { Oxy. 8 }	Sodium 23·3	Soda { Sod. 23·3 } { Oxy. 8 }	Hydrogen 1

or in symbols,



Thus it appears that single equivalents of water, sulphuric acid, and chloride of sodium, yield sulphate of soda and hydrochloric acid. The water of the sulphuric acid is essential; so much so, indeed, that chloride of sodium is not decomposed at all by anhydrous sulphuric acid.

Hydrochloric acid may be generated by the direct union of its elements. When equal measures of chlorine and hydrogen are mixed together, and an electric spark is passed through the mixture, instantaneous combination takes place, heat and light are emitted, and hydrochloric acid is generated. A similar effect is produced by flame, by a red-hot body, and by spongy platinum. Light also causes them to unite. A mixture of the two gases may be preserved without change in a dark place; but if exposed to the diffused light of day, gradual combination ensues, which is completed in the course of 24 hours. The direct solar rays produce,

like flame and electricity, sudden inflammation of the whole mixture, accompanied with explosion; and, according to Brande, the vivid light emitted by charcoal intensely heated by galvanic electricity acts in a similar manner.

This acid is most commonly used in the form of a concentrated aqueous solution, which is made by transmitting a current of the gas into water as long as any of it is absorbed. All the Pharmacopœias give directions for conducting the process. That adopted by the Edinburgh College is practically good. The proportions they recommend are equal weights of sea-salt, water, and sulphuric acid, more acid being purposely employed than is sufficient to form a neutral sulphate with the soda, so that the more perfect decomposition of the sea-salt may be insured. The acid, to prevent too violent effervescence at first, is mixed with one-third of the water; and when the mixture has cooled, it is poured upon the salt previously introduced into a glass retort. The distillation is continued to dryness; and the gas, as it escapes, is conducted into the remainder of the water. The theory of the process has been already explained. The residue is a mixture of sulphate and bisulphate of soda. The sp. gr. of the acid solution obtained by this process is 1.170.

Prop.—It is a colourless gas, has a pungent odour and an acid taste. Under a pressure of 40 atmospheres, and at the temperature of 50°, it is liquid. Sp. gr. 1.2695. It is quite irrespirable, exciting violent spasm of the glottis; but when diluted with air, it is far less irritating than chlorine. All burning bodies are extinguished by it, nor is the gas itself inflammable.

It is not chemically changed by mere heat. It is readily decomposed by galvanism, hydrogen appearing at the —, and chlorine at the + pole. It is also decomposed by ordinary electricity. The decomposition, however, is incomplete; for though one electric spark resolves a portion of the gas into its elements, the next shock in a great measure effects their reunion. It is not affected by oxygen under common circumstances; but if a mixture of oxygen and hydrochloric acid gases is electrified, the oxygen unites with the hydrogen of the acid to form water, and chlorine is set at liberty. For this and the preceding fact we are indebted to the researches of Henry.

One of the most striking properties of hydrochloric acid gas is its powerful attraction for water. A dense white cloud appears

whenever it escapes into the air, owing to its combining with the aqueous vapour of the atmosphere. A piece of ice put into a jar full of the gas confined over mercury liquefies on the instant, and the whole of the gas disappears in the course of a few seconds. On opening a long wide jar of hydrochloric acid gas under water, the absorption of the gas takes place so instantaneously, that the water is forced up into the jar with the same violence as into a vacuum. Considerable increase of temperature takes place during the absorption, and therefore the apparatus should be kept cool by ice. Davy states (*Elements*, p. 252) that water at the temperature of 40° absorbs 480 times its volume of the gas, and that the solution has a sp. gr. of 1.2109. Thomson finds that one cubic inch of water at 69° absorbs 418 cubic inches of gas, and occupies the space of 1.34 cubic inch. The solution has a sp. gr. of 1.1958, and one cubic inch of it contains 311.04 cubic inches of hydrochloric acid gas. The quantity of real acid contained in solutions of different densities may be determined by ascertaining the quantity of pure marble dissolved by a given weight of each. Every 50.6 grains of marble correspond to 36.42 of real acid. The following table from Thomson's "*Principles of Chemistry*," is constructed according to this rule. The first and second columns show the atomic constitution of each acid.

Table exhibiting the Specific Gravity of Muriatic Acid of determinate Strengths.

Atoms of Acid.	Atoms of Water.	Real Acid in 100 of the liquid.	Specific Gravity.	Atoms of Acid.	Atoms of Water.	Real Acid in 100 of the liquid.	Specific Gravity.
1	6	40.659	1.203	1	14	22.700	1.1060
1	7	37.000	1.179	1	15	21.512	1.1008
1	8	33.945	1.162	1	16	20.442	1.0960
1	9	31.346	1.149	1	17	19.474	1.0902
1	10	29.134	1.139	1	18	18.590	1.0860
1	11	27.206	1.1285	1	19	17.790	1.0820
1	12	25.517	1.1197	1	20	17.051	1.0780
1	13	24.026	1.1127				

Hydrochloric acid of commerce has a yellow colour, and is always impure. Its usual impurities are nitric acid, sulphuric acid, and oxide of iron. The presence of nitric acid may be inferred if the hydrochloric acid has the property of dissolving gold leaf. Iron may be detected by ferrocyanuret of potassium, and sulphuric acid by chloride of barium, the suspected hydrochloric acid being previously diluted with three or four parts of water. The presence of

nitric acid is provided against, by igniting the sea-salt, as recommended by the Edinburgh College, in order to decompose any nitre which it may contain. The other impurities may be avoided by employing Woulfe's Apparatus. A few drachms of water are put into the first bottle to retain the chloride of iron and sulphuric acid which pass over, and the hydrochloric acid gas is condensed in the second.

A strong solution of pure hydrochloric acid is a colourless liquid, which emits white vapours when exposed to the air, is intensely sour, reddens litmus paper strongly, and neutralizes alkalies. It combines with water in every proportion, and causes increase of temperature when mixed with it, though in a much less degree than sulphuric acid. It freezes at -60° F.; and boils at 110° , or a little higher, giving off pure hydrochloric acid gas in large quantity.

Hydrochloric acid is decomposed by substances which yield oxygen readily. Thus several peroxides, such as those of manganese, cobalt, and lead, effect its decomposition. Chloric, iodic, bromic, nitric, and selenic acids act on the same principle. A mixture of nitric and hydrochloric acids, in the ratio of one measure of the former to two of the latter, has long been known under the name of *Aqua regia*, as a solvent for gold and platinum. When these acids are mixed together, the solution instantly becomes yellow; and on heating the mixture, pure chlorine is evolved, and the colour of the solution deepens. On continuing the heat, chlorine and nitrous acid vapours are disengaged. At length the evolution of chlorine ceases, and the residual liquid is found to be a solution of hydrochloric and nitrous acids, which is incapable of dissolving gold. The explanation of these facts is, that nitric and hydrochloric acids decompose one another, giving rise to the production of water and nitrous acid, and the separation of chlorine; while hydrochloric and nitrous acids may be heated together without mutual decomposition. It is hence inferred that the power of nitrohydrochloric acid in dissolving gold is owing to the chlorine which is liberated. (Davy in the Quarterly Journal, vol. i.)

Hydrochloric acid is distinguished by its odour, volatility, and strong acid properties. With nitrate of oxide of silver it yields the same precipitate as chlorine; but no chloric acid is generated, because the oxygen of the oxide of silver unites with the hydrogen of the hydrochloric acid, and the chlorine in consequence is entirely precipitated. Notwithstanding that nitrate of oxide of silver yields

the same precipitate with chlorine and hydrochloric acid; there is no difficulty in distinguishing between them; for the bleaching property of the former is a sure ground of distinction.

The composition of hydrochloric acid has been determined by Davy, and Gay-Lussac and Thenard. Their experiments concur in proving that chlorine and hydrogen unite in equal volumes, and that the hydrochloric acid, which is the sole and constant product, occupies the same space as the gases from which it is formed. From these facts the composition of hydrochloric acid is easily inferred. For, as

	Grains
50 cubic inches of Chloride weigh	38.299
50 " " of Hydrogen	1.0699
100 C. I. of Hydrochloric acid gas must weigh	39.3689.

These numbers are in the ratio of 1 to 35.84, being nearly that of single eq. of hydrogen and chlorine. Hence its eq. is 36.42; eq. vol. = 100; symb. H + Cl, or HCl.

COMPOUNDS OF CHLORINE AND OXYGEN.

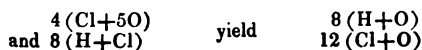
The leading character of these compounds is derived from the circumstance that chlorine and oxygen, the attraction of which for most elementary substances is so energetic, have but a feeble affinity for each other. These principles, consequently, are never met with in nature in a state of combination. Indeed, they cannot be made to combine directly; and when they do unite, very slight causes effect their separation. Chemists have long been doubtful as to the exact number of the compounds of chlorine and oxygen. The recent labours of Balard and Marlen have established the existence of four, all of which they have shown to possess acid properties. Their names and constitutions are given in the subjoined table.

	By weight.		By volume.	
	Chl.	Oxy.	Chl.	Oxy.
Hypochlorous acid	35.42	8	2	1
Chlorous acid	35.42	32	2	4
Chloric acid	35.42	40	2	5
Perchloric acid	35.42	56	2	7

According to the practice of most British chemists, two volumes of chlorine, as also two volumes of hydrogen and of nitrogen, are considered as respectively corresponding to one equivalent or one atom; whereas one volume of oxygen corresponds to one equivalent. Berzelius with many Continental chemists, considering the atoms of

all elements to possess the same volume, regard the four preceding compounds as composed of 2 atoms or 2 eqs. of chlorine combined with 1, 4, 5, and 7 atoms or eqs. of oxygen.

Hypochlorous Acid.—*Hist. and Prep.*—Davy in 1811 discovered a gaseous compound, which was described by him in the Philosophical Transactions of the same year under the name of Euchlorine. This gas, which until recently has been considered to be the protoxide of chlorine, is made by the action of hydrochloric acid on the chlorate of potassa; and its production is explicable by the fact, that hydrochloric and chloric acids mutually decompose each other. When hydrochloric acid and chlorate of potassa are mixed together, more or less of the potassa is separated by the hydrochloric from the chloric acid, and the latter being set at liberty, reacts on free hydrochloric acid. The result depends upon the relative quantities of the materials. If hydrochloric acid be in excess, the chloric acid undergoes complete decomposition. For each eq. of chloric acid, 5 eq. of hydrochloric acid are decomposed: the 5 eq. of oxygen, contained in the former, unite with the hydrogen of the latter, producing 5 eq. of water; while the chlorine of both acids is disengaged. If, on the contrary, chlorate of potassa be in excess, the chloric acid is deprived of part of its oxygen only; the products are water and the euchlorine of Davy. The chloric and hydrochloric acids react on each other in the ratio of 1 eq. to 2, or what is the same thing, in that of 4 eq. to 8 eq.; thus



The gas thus obtained, though containing chlorine and oxygen in the ratio of atom to atom, is not, as was supposed by Davy, a distinct compound, but is a mixture of chlorine and chlorous acid. For this fact, which has long been suspected, we are indebted to the researches of Soubeiran. On transmitting a stream of euchlorine through a tube nearly full of calomel, the free chlorine is readily absorbed; on subsequently exploding the purified gas, he obtained one volume of chlorine to two volumes of oxygen, being the exact composition of chlorous acid. The product of the last decomposition is therefore $3(\text{Cl} + 4\text{O})$ and 9Cl , and not $12(\text{Cl} + \text{O})$. The experiments of Soubeiran have been confirmed by the discoveries of Balard.

If a stream of chlorine gas be passed into a solution of the pure alkalies, or be allowed to act upon the alkaline earths in the form

of hydrates, a bleaching substance is procured which has been commonly viewed as a direct compound of chlorine and an alkaline base. It consists, however, according to Ballard, of a mixture of a metallic chloride and the hypochloride of the alkali employed (An. de Ch. et Ph. lvii. 225). The process recommended for obtaining the pure acid is to pour into bottles filled with chlorine gas peroxide of mercury in fine powder, and mixed with twice its weight of distilled water: by brisk agitation the chlorine is rapidly and completely absorbed, if a slight excess of the peroxide be used. By this process one portion of the peroxide of mercury, Hg O_2 , is decomposed, both its constituents combining with chlorine, the mercury forming corrosive sublimate, Hg Cl_2 , and the oxygen hypochlorous acid. The latter remains in solution in the water, while the former, by combining with undecomposed peroxide of mercury, forms the sparingly soluble oxychloride of mercury, which is separated by filtration. The hypochlorous acid being volatile, is obtained in a pure but diluted state by distillation. The temperature which is used for this purpose should be kept considerably below 212° , as the hypochlorous acid decomposes rapidly at that heat: the process is, therefore, best performed under reduced pressure. A more concentrated solution of the acid is obtained by submitting the first products to a second distillation.

Prop.—As thus obtained, hypochlorous acid is a transparent liquid of a slightly yellow colour when concentrated. Its odour is strong and penetrating, and different though somewhat similar to chlorine. Its action on the skin is exceedingly active, the effect being similar to but greater than that produced by nitric acid. It is a highly bleaching compound. In a concentrated state it is very unstable, a slow decomposition taking place at common temperatures, by which chlorine is evolved and chloric acid produced. This change is promoted by light, and is effected almost instantly by exposure for a few moments to the direct rays of the sun. It is also decomposed by agitation with angular bodies; and on throwing into the acid a portion of pounded glass, a brisk effervescence is observed from the escape of chlorine.

It is one of the most powerful oxidizing agents. Its action in this respect, however, is various, and is principally observed in relation to the simple non-metallic elements. Thus sulphur and phosphorus are readily brought to their highest state of oxidation, and even selenium is converted into selenic acid, an effect which the

nitric acid cannot accomplish. Iodine and bromine are also instantly changed into iodic and bromic acids. Its action on the more perfect metals, on the contrary, is slight: iron and silver, however, are remarkable exceptions to this rule; for when either of them is brought in a finely divided state in contact with hypochlorous acid, the latter suffers instantaneous decomposition. When iron is used, it is oxidized at the expense of the acid, and chlorine is evolved; with silver the oxygen escapes, and the chlorine unites exclusively with the metal. The decomposition of hypochlorous acid may also be produced by metallic mercury, but the decomposition is unattended by the evolution of either gas. Both the chloride and oxide of mercury are produced, and instantly unite to form the oxychloride.

Balard has also succeeded in obtaining hypochlorous acid in the gaseous form. A small quantity of a concentrated solution is introduced into a bell jar over mercury, and fragments of dry nitrate of lime are successively added. The nitrate of lime being highly deliquescent, unites with the water, and the acid gas escapes with effervescence: the presence of the saline solution is essential, as it prevents the decomposition of the gas by the mercury. The gas is of a yellowish green colour, and is very similar to chlorine in appearance. It unites rapidly by water, which absorbs at least 100 times its own volume of gas. It detonates by a slight increase of temperature; and though less explosive than the chlorous acid, there is a probability of an accident in transferring it from one vessel to another. The results of explosion are oxygen and chlorine; and Balard found that 100 measures produced 100 of chlorine and 50 of oxygen. From these data its sp. gr. is 3.0212; its eq.

43.42; eq. vol. = 100; symb. $\text{Cl} + \text{O}$, Cl or ClO .

Chlorous Acid.—Hist. and Prep.—This compound was discovered by Davy in 1815 (Phil. Trans.), and soon after by Count Stadion of Vienna. It is formed by the action of sulphuric acid on chlorate of potassa. A quantity of this salt not exceeding 50 or 60 grains is reduced to powder, and made into a paste by the addition of strong sulphuric acid. The mixture, which acquires a deep yellow colour, is placed in a glass retort, and heated by warm water, the temperature of which is kept under 212°F . A bright yellowish green gas of a richer colour than chlorine is disengaged, which has an aromatic odour without any smell of chlorine, is absorbed rapidly by water, to which it communicates its tint. This

gas, which has long been described as the peroxide of chlorine, must now be called chlorous acid, as it has been shown to possess acid properties, and to form definite compounds with the alkaline bases.

The chemical changes which take place in the process are explained in the following manner. The sulphuric acid decomposes some of the chlorate of potassa, and sets chloric acid at liberty. The chloric acid, at the moment of separation, resolves itself into peroxide of chlorine and oxygen; the last of which, instead of escaping as free oxygen gas, goes over to the acid of some undecomposed chlorate of potassa, and converts it into perchloric acid. The products are bisulphate and perchlorate of potassa, and chlorous acid. It is most probable, from the data contained in the preceding table, that every 3 eq. of chloric acid yield 1 eq. of perchloric acid and 2 eq. of chlorous acid.

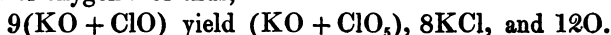
Prop.—Chlorous acid unites readily with the alkalies and alkaline earth, forming salts which are more stable than those of the hypochlorous acid. They are produced by transmitting the gas into the alkaline solutions, which may thus be rendered perfectly neutral (Martens, *An. de Ch. et Ph.* lxi. 293). All the salts hitherto examined are soluble in water, and are possessed, like the acid itself, of bleaching properties. The neutral salts pass readily into a metallic chloride and chlorate of the base, particularly such as the chloride of potash, which form a sparingly soluble chlorate. This change does not so readily ensue when alkali is in excess. The proportion in which the chloride and chlorate are produced indicate that 6 eq. of chlorite are decomposed, by which 1 eq. of metallic chloride and 5 eq. of chlorate are produced: thus 6KO ClO_4 yields KCl and 5KO ClO_5 . The solution of the pure acid gradually yields chloric acid and chlorine. It is a powerful oxidizing agent, and in this respect is very similar to the hypochlorous acid. It causes a precipitate with nitrate of silver; but it is best recognized by the evolution of chlorous acid gas on the addition of an acid to its salts.

Phosphorus takes fire when introduced into the gas, and occasions an explosion. It explodes violently when heated to a temperature of 212° , emits a strong light, and undergoes a greater expansion than protoxide of chlorine. According to Davy, whose result is confirmed by Gay-Lussac, 40 measures of the gas occupy after explosion the space of 60 measures; and of these, 20 are

chlorine and 40 oxygen. The peroxide is therefore composed of 35.42 parts, or 1 eq. of chlorine, united with 32 or 4 eq. of oxygen; and its sp. gr. must be 2.3375.

Its eq. is 67.42; eq. vol. = 100; symb. $\text{Cl} + 4\text{O}$, Cl , or ClO_4 .

Chloric Acid.—Prep.—If a current of chlorine gas be transmitted into a strong solution of pure potassa, a portion of the alkali is decomposed, and chloride of potassium and hypochlorite of potassa are generated. On bringing the solution to the boiling point, the latter salt is decomposed. The changes which occur are complicated, and give rise to the evolution of oxygen, and the formation of chlorate of potassa and chloride of potassium. According to the experiments of Morin and Soubeiran, which accord entirely with the observations of Balard, 9 eq. of hypochlorite of potassa produce 1 eq. of chlorate of potassa, 8 eq. of chloride of potassium, and 12 eq. of oxygen: or thus,



Hence for every eq. of chlorate, 17 eq. of chloride are formed.

When to a dilute solution of chlorate of baryta a quantity of weak sulphuric acid, exactly sufficient for combining with the baryta, is added, the insoluble sulphate of baryta subsides, and pure chloric acid remains in the liquid. This acid, the existence of which was originally observed by Mr. Chenevix, was first obtained in a separate state by Gay-Lussac.

Prop.—Chloric acid reddens vegetable blue colours, has a sour taste, and forms neutral salts, called *chlorates*, (formerly *hyperoxymuriates*), with alkaline bases. It possesses no bleaching properties, a circumstance by which it is distinguished from chlorine, hypochlorous, and chlorous acids. It gives no precipitate in solution of nitrate of oxide of silver, and hence cannot be mistaken for hydrochloric acid. Its solution may be concentrated by gentle heat till it acquires an oily consistence without decomposition: in this state of highest concentration it acquires a yellowish tint, emits an odour of nitric acid, sets fire to paper and other dry organic matter, and converts alcohol into acetic acid. When sharply heated in a retort, part of the acid is resolved into chlorine and oxygen; but another portion, acquiring oxygen from that which is decomposed, is converted into perchloric acid, and then passes over into the receiver in the form of a dense colourless liquid (Serullas). Chloric acid is easily decomposed by deoxidizing agents. Sulphurous acid,

for instance, deprives it of oxygen, with formation of sulphuric acid and evolution of chlorine. By the action of hydrosulphuric acid, water is generated, while sulphur and chlorine are set free. The power of hydrochloric acid in effecting its decomposition has already been explained.

Chloric acid is readily known by forming a salt with potassa which crystallizes in tables and has a pearly lustre, decomposes like nitre when flung on burning charcoal, and yields peroxide of chlorine by the action of concentrated sulphuric acid. Chlorate of potassa, like most of the chlorates, gives off pure oxygen when heated, and leaves a residue of chloride of potassium. By this mode Gay-Lussac ascertained the composition of chloric acid, as stated in the preceding table. (An. de Chimie, xcii.)

Its eq. is 75.42; symb. $\text{Cl} + 5\text{O}$, Cl , or ClO_5 .

Perchloric Acid.—The saline matter which remains in the retort after forming chlorous acid, is a mixture of perchlorate and bisulphate of potassa; and by washing it with cold water, the bisulphate is dissolved, and the perchlorate is left. Perchloric acid may be prepared from this salt by mixing it in a retort with half its weight of sulphuric acid, diluted with one-third of water, and applying heat to the mixture. At the temperature of about 284° F. white vapours rise, which condense as a colourless liquid in the receiver. This is a solution of perchloric acid.

The existence of perchloric acid was first ascertained by Count Stadion, who found it to be a compound of 2 volumes or 1 eq. of chlorine and 7 of oxygen; and this view of its constitution has been confirmed by Gay-Lussac, Serullas, and Mitscherlich. (An. de Ch. et Ph. viii. ix. xlv. 297, and xlix. 113.) According to Serullas, it is a very stable compound: it may be heated with hydrochloric or sulphuric acid without change, does not set fire to organic substances, and is not decomposed by alcohol. When concentrated it has a density of 1.65, in which state it emits vapour when exposed to the air, absorbs hygrometric moisture powerfully, and boils at 392° F. By admixture with strong sulphuric acid and distilling, Serullas obtained it in the solid form, both massive and in elongated prisms. It hisses when thrown into water, like red-hot iron when quenched.

Of all the salts of perchloric acid, that with potassa is the most insoluble, requiring 65 times its weight of water at 60° for solution.

This salt is readily and safely formed by adding chlorate of potassa, well dried and in fine powder, in small portions at a time, to an equal weight of concentrated sulphuric acid, gently warmed in an open vessel. The chlorous acid gas escapes without danger, and the chlorate is entirely converted into perchlorate and bisulphate of potassa, the latter of which, being very soluble, is easily removed by cold water. Serullas finds that chlorate of potassa, when decomposed by a low heat, is converted into chloride of potassium and perchlorate of potassa; but the temperature must be carefully managed, otherwise the perchlorate itself would be resolved into oxygen and chloride of potassium. The perchlorate thus procured is purified by solution in hot water and crystallization. It is distinguished from chlorate of potassa by not acquiring a yellow tint on the addition of hydrochloric acid. The primary form of its crystals, according to Mitscherlich, is a right rhomboidal prism isomorphous with permanganate of potassa.

Its eq. is 91.42; symb. $\text{Cl} + 7\text{O}$, Cl , or ClO_7 .

Quadrochloride of Nitrogen.—*Hist. and Prep.*—This compound was discovered by Dulong in 1811. Its elements have a feeble mutual affinity, and do not unite when presented to each other in their gaseous form. The condition which leads to their union is the decomposition of ammonia by chlorine, during which hydrochloric acid is generated by chlorine combining with the hydrogen of ammonia; while the nitrogen of that alkali, in its nascent state, enters into combination with another portion of chlorine. A convenient mode of preparing the quadrochloride of nitrogen is the following. An ounce of hydrochlorate of ammonia is dissolved in 12 or 16 ounces of hot water; and when the solution has cooled to the temperature of 90° , a glass bottle with a wide mouth, full of chlorine, is inverted in it. The solution gradually absorbs the chlorine, and acquires a yellow colour; and in about 20 minutes globules of a yellow fluid are seen floating like oil upon its surface, which, after acquiring the size of a small pea, sink to the bottom of the liquid. The drops of the chloride, as they descend, should be collected in a small saucer of lead, placed for that purpose under the mouth of the bottle. It is also readily obtained by suspending a fragment of sal-ammonia in a solution of hypochlorous acid.

Prop.—It is one of the most explosive compounds yet known,

having been the cause of serious accidents both to its discoverer and to Davy. (Phil. Trans. 1818; An. de Ch. lxxxvi.) Its specific gravity is 1.658. It does not congeal in the intense cold produced by a mixture of snow and salt. It may be distilled at 160°; but at a temperature between 200° and 212° it explodes. It appears from the investigation of Messrs. Porrett, Wilson, and Kirk, that its mere contact with some substances of a combustible nature causes detonation even at common temperatures. This result ensues particularly with oils, both volatile and fixed. I have never known olive oil fail in producing the effect. The products of the explosion are chlorine and nitrogen. (Nicholson's Journal, xxxiv.)

Sir H. Davy analyzed chloride of nitrogen by means of mercury, which unites with chlorine, and liberates the nitrogen. He inferred from his analysis that its elements are united in the proportion of four measures of chlorine to one of nitrogen; and it hence follows that, by weight, it consists of 4 eq. of chlorine and 1 eq. of nitrogen.

Perchloride of Carbon.—*Hist. and Prep.*—The discovery of this compound is due to Mr. Faraday. When olefiant gas (a compound of carbon and hydrogen) is mixed with chlorine, combination takes place between them, and an oil-like liquid is generated, which consists of chlorine, carbon, and hydrogen. On exposing this liquid in a vessel full of chlorine gas to the direct solar rays, the chlorine acts upon and decomposes the liquid, hydrochloric acid is set free, and the carbon, at the moment of separation, unites with the chlorine. (Phil. Trans. 1821.)

Prop.—Perchloride of carbon is solid at common temperatures, has an aromatic odour approaching to that of camphor, is a non-conductor of electricity, and refracts light very powerfully. Its sp. gr. is exactly double that of water. It fuses at 320°, and after fusion it is colourless and very transparent. It boils at 360°, and may be distilled without change, assuming a crystalline arrangement as it condenses. It is sparingly soluble in water, but dissolves in alcohol and ether, especially by the aid of heat. It is soluble also in fixed and volatile oils.

It burns with a red light when held in the flame of a spirit-lamp, giving out acid vapours and smoke; but the combustion ceases as soon as it is withdrawn. It burns vividly in oxygen gas. Alkalies do not act upon it; nor is it changed by the stronger acids, such as the hydrochloric, nitric, or sulphuric acids, even with the aid of heat. When its vapour, mixed with hydrogen, is transmitted

through a red-hot tube, charcoal is separated, and hydrochloric acid gas evolved. On passing its vapour over the peroxides of metals, such as that of mercury and copper, heated to redness, a chloride of the metal and carbonic acid are generated. Protoxides, under the same treatment, yield carbonic oxide gas and metallic chlorides. Most of the metals decompose it also at the temperature of ignition, uniting with its chlorine, and causing deposition of charcoal.

The composition of the perchloride of carbon was inferred by Faraday from the proportions of chlorine and olefiant gas employed in its production, and from the quantity of chloride of copper and carbonic acid generated when its vapour was transmitted over oxide of copper at a red heat.

Its eq. is 118.50; symb. $2C + 3Cl$, or $C_2 Cl_3$.

Protochloride of Carbon.—When the vapour of the perchloride is passed through a red-hot glass or porcelain tube, filled with fragments of rock crystal to increase the quantity of heated surface, partial decomposition occurs, chlorine gas escapes, and a vapour which, analyzed by Faraday by means of oxide of copper, proved to be protochloride of carbon. At common temperatures it is a limpid colourless liquid, which has a density of 1.5526, does not congeal at $0^\circ F$, and at 160° or 170° is converted into vapour. It may be distilled repeatedly without change; but when exposed to a red heat, some of it is resolved into its elements. In its chemical relations it is very analogous to perchloride of carbon.

Its eq. is 41.54; symb. $C + Cl$, or $C Cl$.

Dichloride of Carbon.—The only sample of this substance yet obtained was brought from Sweden by M. Julin, and is said to have been formed during the distillation of nitric acid from crude nitre and sulphate of iron. It occurs in small, soft, adhesive fibres of a white colour, which have a peculiar odour, somewhat resembling spermaceti. It fuses on the application of heat, and boils at a temperature between 350° and $450^\circ F$. At 250° it sublimes slowly, and condenses again in the form of long needles. It is insoluble in water, acids, and alkalis; but is dissolved by hot oil of turpentine or by alcohol, and forms acicular crystals as the solution cools. It burns with a red flame, emitting much smoke and fumes of hydrochloric acid gas.

The nature of this substance is shown by the following circumstances. When its vapour is exposed to a red heat, evolution of chlorine gas ensues, and charcoal is deposited. A

similar deposition of charcoal is produced (by heating it with phosphorus, iron, or tin, and a chloride is formed at the same time. Potassium burns vividly in its vapour with formation of chloride of potassium and separation of charcoal. On detonating a mixture of its vapour with oxygen gas over mercury, a chloride of that metal and carbonic acid are generated. By these means Phillips and Faraday ascertained its composition (Ann. of Phil. xviii. 150). Its eq. is 47.66; symb. $2C + Cl$, or $C_2 Cl$.

Dichloride of Sulphur.—This compound was discovered in the year 1804 by Thomson,* and was afterwards examined by Barthollet.† It is most conveniently prepared by passing a current of chlorine gas over flowers of sulphur gently heated, until nearly all the sulphur disappears. Direct combination ensues, and the product, distilled off from uncombined sulphur, is obtained under the form of a liquid which appears red by reflected, and yellowish green by transmitted light. Its density is 1.687. It is volatile below 200° , boils at 280° , yielding vapour which has a density of 4.70, and condenses again without change in cooling. When exposed to the air it emits acrid fumes, which irritate the eyes powerfully, and have an odour somewhat resembling sea-weed, but much stronger. Dry litmus paper is not reddened by it, nor does it unite with alkalis. It acts with energy on water:—mutual decomposition ensues, with formation of hydrochloric and hyposulphurous acids, and deposit of sulphur, by which the water is rendered cloudy. From a recent analysis by Rose it consists of 35.42 parts or 1 eq. of chlorine and 32.2 parts or 2 eq. of sulphur (Pog. Ann. xlii. 431). Its eq. is 67.62; symb. $2S + Cl$, or $S_2 Cl$. Rose maintains that the preceding is the only chloride of sulphur, arguing that the chloride analyzed by Davy was merely dichloride of sulphur holding chlorine in solution. Dumas, on the other hand, contends, that when sulphur is acted on by excess of chlorine, a chloride of sulphur is really obtained, which is apt to retain traces of the dichloride, and can only be purified by repeated distillation at about $140^\circ F$. This chloride is a liquid of a deep reddish brown tint, and has a density of 1.62. It boils at 145° , and the density of its vapour is between 3.67 and 3.70. By decomposition in water it should yield hydrochloric and hyposulphurous acids (Ann. de Ch. et Ph. xlix. 205.).

Perchloride of Phosphorus.—There are two definite compounds of chlorine and phosphorus, the nature of which was first satisfac-

* Nicholson's Journal, vol. vi.

† Mémoires d'Arcueil, vol. i.

torily explained by Davy (Elements, p. 290). When phosphorus is introduced into a jar of dry chlorine, it inflames, and on the inside of the vessel a white matter collects, which is *perchloride of phosphorus*. It is very volatile; a temperature much below 212° being sufficient to convert it into vapour. Under pressure it may be fused, and it yields transparent prismatic crystals in cooling.

Water and perchloride of phosphorus mutually decompose each other; and the sole products are hydrochloric and phosphoric acids. Now in order that these products should be formed, consistently with the constitution of phosphoric acid, as stated at page 317, the perchloride must consist of 31.4 parts or 2 eq. of phosphorus, and 177.1 parts or 5 eq. of chlorine. One equivalent of the chloride and 5 eq. of water will then mutually decompose each other without any element being in excess, and yield 1 eq. of phosphoric, and 5 eq. of hydrochloric acid. This proportion is not far from the truth; for according to Davy, one grain of phosphorus is united in the perchloride with six of chlorine.

Its eq. is 206.4; symb. $2P + 5Cl$, or $P_2 Cl_5$.

Sesquichloride of Phosphorus may be made either by heating the perchloride with phosphorus, or by passing the vapour of phosphorus over corrosive sublimate contained in a glass tube. It is a clear liquid like water, of sp. gr. 1.45; emits acid fumes when exposed to the air, owing to the decomposition of watery vapour; but when pure it does not redden dry litmus paper. On mixing it with water, mutual decomposition ensues, heat is evolved, and a solution of hydrochloric and phosphoric acids is obtained. It hence appears to consist of 31.4 parts or 2 eq. of phosphorus, and 106.26 parts or 3 eq. of chlorine. Its eq. is 137.66; symb. $2P + 3Cl$, or $P_2 Cl_3$.

When hydrosulphuric acid gas is transmitted through a vessel containing perchloride of phosphorus, hydrochloric acid is disengaged, and a liquid produced which, according to Serullas, is a compound of three equivalents of chlorine, one of phosphorus, and one of sulphur. (An. de Ch. et Ph. xlii. 25.)

Chlorocarbonic Acid Gas.—*Hist. and Prep.*—This compound was discovered in 1812 by Davy, who described it in the Philosophical Transactions for that year, under the name of *phosgene gas*. (From $\phi\alpha\varsigma$ light, and $\gamma\epsilon\upsilon\upsilon\epsilon\iota\nu$ to produce.) It is made by exposing a mixture of equal measures of dry chlorine and carbonic oxide gases to sunshine, when rapid but silent combination ensues, and they contract to one half their volume. Diffused day-light also

effects their union slowly; but they do not combine at all when the mixture is wholly excluded from light.

Prop.—It is colourless gas, has a strong odour, and reddens dry litmus paper. It combines with four times its volume of ammoniacal gas, forming a white solid salt; so that it possesses the characteristic property of acids. It is decomposed by contact with water. One equivalent of each compound undergoes decomposition; and as the hydrogen of the water unites with chlorine, and its oxygen with carbonic oxide, the products are carbonic and hydrochloric acids. When tin is heated in this gas, chloride of tin is generated, and carbonic oxide gas set free, which occupies exactly the same space as the chlorocarbonic acid which was employed. A similar change occurs when it is heated in contact with antimony, zinc, or arsenic.

As chlorocarbonic acid gas contains its own volume of each of its constituents, it follows that 100 cubic inches of that gas at the standard temperature and pressure must weigh 106.806 grains; namely, 76.599 of chlorine added to 30.207 of carbonic oxide. Its sp. gr. is therefore 3.4427, and it consists of 35.42 parts or 1 eq. of chlorine, and 14.15 parts or 1 eq. of carbonic oxide.

Its eq. is 49.54; symb. $C + O + Cl$, or $CO Cl$.

Tetrachloride of Boron.—Davy noticed that recently prepared boron takes fire spontaneously in an atmosphere of chlorine, and emits a vivid light; but he did not examine the product. Berzelius remarked, that if the boron has been previously heated, whereby it is rendered more compact, the combustion does not take place till heat is applied. This observation led him to expose boron, thus rendered dense, in a glass tube to a current of dry chlorine; and to heat it gently as soon as the atmospheric air was completely expelled, in order to commence the combustion. The resulting compound proved to be a colourless gas; and on collecting it over mercury, which absorbed free chlorine, he procured the chloride of boron in a state of purity. This gas is rapidly absorbed by water; but double decomposition takes place at the same instant, giving rise to hydrochloric and boracic acids as the sole products: from this fact is inferred the composition of the chloride; for 1 eq. of tetrachloride of boron or $B + 3 Cl$, and 3 eq. of water or $3 (H + O)$; correspond to 1 eq. of boracic acid or $B + 3 O$, and 3 eq. of hydrochloric acid or $3 (H + Cl)$. The watery vapour of the atmosphere occasions a similar change; so that when the gas is mixed with air

containing hygrometric moisture, a dense white cloud is produced. The sp. gr. of the gas, according to Dumas, is 3.942. It is soluble in alcohol, and communicates to it an ethereal odour, apparently by the action of hydrochloric acid. It unites with ammoniacal gas, forming a fluid volatile substance, the nature of which is unknown. 44 (Annals of Phil. xxvi. 129.)

Dumas finds that chloride of boron may be generated by the action of dry chlorine on a mixture of charcoal and boracic acid, heated to redness in a porcelain tube. Although neither charcoal nor chlorine can, when acting alone, decompose boracic acid, they do so readily by their united effort. According to Dumas, two volumes of chloride of boron, and three of carbonic oxide gas are formed. From these data chloride of boron may be considered as composed of 3 eq. vol. of chlorine and 1 eq. vol. of boron condensed into two volumes. Its sp. gr. is 4.079 (Dumas).

Despretz also appears to have invented a similar process. (Philos. Magazine and Annals, i. 469.)

Its eq. is 117.16; eq. vol. = 200; symb. $B + 3Cl$. or BCl_3 .

Tetrachloride of Silicon.—When silicon is heated in a current of chlorine gas, it takes fire, and is rapidly volatilized. The product of the combustion condenses into a liquid, which appears to be naturally colourless, but to which an excess of chlorine communicates a yellow tint. This fluid is very limpid and volatile, and evaporates almost instantaneously in open vessels in the form of a white vapour. It boils at 124° , and bears a cold of zero without becoming solid. It has a suffocating odour not unlike that of cyanogen, and when put into water is converted into hydrochloric and silicic acids, the latter being easily obtained in a gelatinous form. (Berzelius).

It may also be prepared by the method proposed by Oersted, which has been so successfully applied in the formation of other chlorides. It consists in mixing about equal parts of hydrated silicic acid and starch into a paste with oil, heating the mass in a covered crucible so as to char the starch, introducing the mixture in fragments into a porcelain tube, and then transmitting through it a current of dry chlorine gas while the tube is kept at a red heat. The chlorine unites with silicium, while the charcoal and oxygen combine. The volatile chloride is then agitated with mercury to separate the free chlorine, and purified by distillation.

Its eq. is 128.76; symb. $Si + 3Cl$. or $SiCl_3$.

Chloro-nitrous Gas.—When fused chloride of sodium, potassium, or calcium, in powder, is treated with as much strong nitric acid as is sufficient to wet it, mutual decomposition ensues, and a new gas, composed of chlorine and binoxide of nitrogen, is generated. Its discoverer, Mr. E. Davy, describes it as a gas of a pale reddish yellow colour, of an odour similar to that of chlorine, though less pungent, and possessed of bleaching properties. It fumes on exposure to the air, and is freely absorbed by water. It is decomposed by sulphur, phosphorus, mercury, and most metals, and by substances in general which have an affinity for chlorine. It consists, according to Davy, of equal volumes of chlorine and binoxide of nitrogen, united without any condensation.

In the mutual decomposition of chloride of sodium and nitric acid, the products appear to be chloro-nitrous and chlorine gases, and nitrate of soda. Their formation must obviously depend on sodium being oxidized at the expense of nitric acid, while part of the chlorine unites, at the moment of separation from the sodium, with binoxide of nitrogen. (Phil. Mag. ix. 355.) Theoretically, it should be mixed with twice its volume of chlorine, the presence of which must materially obscure the properties of the new gas.

ON THE NATURE OF CHLORINE.

The change of opinion which has gradually taken place among chemists concerning the nature of chlorine, is a remarkable fact in the history of the science. The hypothesis of Berthollet, unfounded as it is, prevailed at one time universally. It explained phenomena so satisfactorily, and in a manner so consistent with the received chemical doctrine, that for some years no one thought of calling its correctness into question. A singular reverse, however, has taken place; and this hypothesis, though it has not hitherto been rigidly demonstrated to be erroneous, has within a short period been generally abandoned, even by persons who, from having adopted it in early life, were prejudiced in its favour. The reason of this will readily appear on comparing it with the opposite theory, and examining the evidence in favour of each.

Chlorine, according to the new theory, is maintained to be a simple body, because, like oxygen, hydrogen, and other analogous substances, it cannot be resolved into more simple parts. It does not indeed follow that a body is simple because it has not hitherto been decomposed; but as chemists have no other mode of estimating

the elementary nature of bodies, they must necessarily adopt this one, or have none at all. Hydrochloric acid, by the same rule, is considered to be a compound of chlorine and hydrogen. For when exposed to the agency of galvanism, it is resolved into these substances; and by mixing the two gases in due proportion, and passing an electric spark through the mixture, hydrochloric acid gas is the product. Chemists have no other kind of proof of the composition of water, of potassa, or of any other compound.

Very different is the evidence in support of the theory of Berthollet. According to that view, hydrochloric acid gas is composed of *absolute muriatic acid* and water or its elements; chlorine consists of *absolute muriatic acid* and oxygen; and *absolute muriatic acid* is a compound of a certain unknown base and oxygen gas. Now all these propositions are gratuitous. For, in the first place, hydrochloric acid gas has not been proved to contain water. Secondly, the assertion that chlorine contains oxygen is opposed to direct experiment, the most powerful deoxidizing agents having been unable to elicit from that gas a particle of oxygen. Thirdly, the existence of such a substance as *absolute muriatic acid* is wholly without proof, and therefore its supposed base is also imaginary.

But this is not the only weak point of the doctrine. Since chlorine is admitted by this theory to contain oxygen, it was necessary to explain how it happens that no oxygen can be separated from it. For instance, on exposing chlorine to a powerful galvanic battery, oxygen gas does not appear at the positive pole, as occurs when other oxidized bodies are subjected to its action; nor is carbonic acid or carbonic oxide evolved, when chlorine is conducted over ignited charcoal. To account for the oxygen not appearing under these circumstances, it was assumed that *absolute muriatic acid* is unable to exist in an uncombined state, and therefore cannot be separated from one substance except by uniting with another. This supposition was thought to be supported by the analogy of certain compounds, such as nitric and oxalic acids, which appear to be incapable of existing except when combined with water or some other substance. The analogy, however, is incomplete; for the decomposition of such compounds, when an attempt is made to procure them in an insulated state, is manifestly owing to the tendency of their elements to enter into new combinations.

Admitting the various assumptions which have been stated, most of the phenomena receive as consistent an explanation by the old as

by the new theory. Thus, when hydrochloric acid gas is resolved by galvanism into chlorine and hydrogen, it may be supposed that *absolute muriatic acid* attaches itself to the oxygen of the water, and forms chlorine; while the hydrogen of the water goes to the opposite pole of the battery. When chlorine and hydrogen enter into combination, the oxygen of the former may be said to unite with the latter; and that hydrochloric acid gas is generated by the water so formed combining with the *absolute muriatic acid* of the chlorine. The evolution of chlorine, which ensues on mixing hydrochloric acid and peroxide of manganese, is explained on the supposition that *absolute muriatic acid* unites directly with the oxygen of the black oxide of manganese.

It will not be difficult, after these observations, to account for the preference shown to the new theory. In an exact science, such as chemistry, every step of which is required to be matter of demonstration, there is no room to hesitate between two modes of reasoning, one of which is hypothetical, and the other founded on experiment. Nor is there, in the present instance, temptation to deviate from the strict logic of the science; for there is not a single phenomenon which may not be fully explained on the new theory, in a manner quite consistent with the laws of chemical action in general.

It was supposed, indeed, at one time, that the sudden decomposition of water, occasioned by the action of that liquid on the compounds of chlorine with some simple substances, constitutes a real objection to the doctrine; but it will afterwards appear, that the acquisition of new facts has deprived this argument of all its force. While nothing therefore can be gained, much may be lost, by adopting the doctrine of Berthollet. If chlorine is regarded as a compound body, the same opinion, though in direct opposition to the result of observation, ought to be extended to iodine and bromine; and as other analogous substances may hereafter be discovered, in regard to which a similar hypothesis will apply, it is obvious that this view, if proper in one case, may legitimately be extended to others. One encroachment on the method of strict induction would consequently open the way to another, and thus the genius of the science would eventually be destroyed.

An able attempt was made some years ago by the late Dr. Murray, to demonstrate the presence of water or its elements as a constituent part of hydrochloric acid gas, and thus to establish the

old theory to the subversion of the new. The arguments which he used, though plausible and ingenious, were successfully combated by Sir H. and Dr. Davy. The only experiment which strictly bears upon the question—that, namely, where hydrochloric acid and ammoniacal gases were mixed together, goes far to demonstrate the absence of combined water in hydrochloric acid gas, and thereby to establish the views of Davy.*

SECTION XIII.

IODINE.

Hist.—IODINE was discovered in the year 1812 by M. Courtois, a manufacturer of saltpetre at Paris. In preparing carbonate of soda from the ashes of sea-weeds, he observed that the residual liquor corroded metallic vessels powerfully; and on investigating the cause of the corrosion, he noticed that sulphuric acid threw down a dark-coloured matter, which was converted by the application of heat into a beautiful violet vapour. Struck with its appearance, he gave some of the substance to M. Clément, who recognised it as a new body, and in 1813 described some of its leading properties in the Royal Institute of France. Its real nature was soon after determined by Gay-Lussac and Davy, each of whom proved that it is a simple non-metallic substance, exceedingly analogous to chlorine.†

Iodine is frequently met with in nature in combination with potassium or sodium. Under this form it occurs in many salt and other mineral springs, both in England and on the Continent. It has been detected in the water of the Mediterranean, in the oyster and some other marine molluscous animals, in sponges, and in most kinds of sea-weed. In some of these productions, such as the *Fucus serratus* and *Fucus digitatus*, it exists ready formed, and according to Fyfe (Edin. Philos. Journal, i. 254) may be separated by the action of water; but in others it can be detected only after incineration. Marine animals and plants doubtless derive from the sea the iodine which they contain. Vauquelin found it also in the

* In Nicholson's Journal, vols. xxxi. xxxii. and xxxiv. Edinburgh Philos. Trans. vol. viii. and Philos. Trans. for 1818.

† The original papers on this subject are in the Annales de Chimie, vols. lxxxviii. xc. and xci.; and in the Philos. Trans. for 1814 and 1815.

mineral kingdom, in combination with silver. (Ann. des Ch. et Ph. xxix.)

Prep.—The iodine of commerce is procured from the limpure carbonate of soda, called kelp, which is prepared in large quantity on the northern shores of Scotland, by incinerating seaweeds. The kelp is employed by soap-makers, for the preparation of carbonate of soda; and the dark residual liquor remaining after that salt has crystallized, contains a considerable quantity of iodine, combined with sodium or potassium. By adding a sufficient quantity of sulphuric acid, hydriodic acid is first generated, and then decomposed. The iodine sublimes when the solution is boiled, and may be collected in cool glass receivers. A more convenient process is to employ a moderate excess of sulphuric acid, and then add to the mixture some peroxide of manganese, which acts on hydriodic in the same way as on hydrochloric acid (page 329), (Phil. Mag. L. Ure). Another method proposed by Soubeiran, is by adding to the ley from kelp a solution made with the sulphates of protoxides of copper and iron in the ratio of one of the former to $2\frac{1}{4}$ of the latter, as long as a white precipitate appears. The diiodide of copper is thus thrown down; and it may be decomposed either by peroxide of manganese alone, or by manganese and sulphuric acid. By means of the former, the iodine passes over quite dry; but a strong heat is requisite.

Prop.—Iodine, at common temperatures, is a soft friable opaque solid of a bluish-black colour, and metallic lustre. It occurs usually in crystalline scales, having the appearance of micaceous iron ore; but it sometimes crystallizes in large rhomboidal plates, the primitive form of which is a rhombic octohedron. The crystals are best prepared by exposing to the air a solution of iodine in hydriodic acid. Its sp. gr. according to Gay-Lussac, is 4.948; but Thomson found it only 3.0844. At 225° it is fused, and enters into ebullition at 347° ; but when moisture is present, it is sublimed rapidly even below the degree of boiling water, and suffers a gradual dissipation at low temperatures. Its vapour is of an exceedingly rich violet colour, a character to which it owes the name of *Iodine*. (From *ἰώδης*, violet-coloured.) This vapour is remarkably dense, its sp. gr. by calculation, page 231, being 8.7011, or 8.716 as directly observed by Dumas. Hence 100 cubic inches, at the standard temperature and pressure, must weigh 269.84 grains.

It is a non-conductor of electricity, and, like oxygen and chlo-

rine) is a conductor of electricity. It has a very acrid taste, and its odour is almost exactly similar to that of chlorine, when much diluted with air. It acts energetically on the animal system as an irritant poison, but is employed medicinally in very small doses with advantage. It is very sparingly soluble in water, requiring about 7000 times its weight of that liquid for solution. It communicates, however, even in this minute quantity, a brown tint to the menstruum. Alcohol and ether dissolve it freely, and the solution has a deep reddish-brown colour.

Iodine possesses an extensive range of affinity. It destroys vegetable colours, though in a much less degree than chlorine. It manifests little disposition to combine with metallic oxides; but it has a strong attraction for the pure metals, and for most of the simple non-metallic substances, producing compounds which are termed *Iodides* or *Iodurets*. It is not inflammable; but under favourable circumstances may, like chlorine, be made to unite with oxygen. A solution of the pure alkalis acts upon it and gives rise to decomposition of water; whether an hypo-iodite and iodide are first produced, as in the case of chlorine, has not yet been determined, but on the application of heat an iodate and iodide are formed.

Pure iodine is not influenced chemically by the imponderables. Exposure to the direct solar rays, or to strong shocks of electricity, does not change its nature. It may be passed through red-hot tubes, or over intensely ignited charcoal, without any appearance of decomposition; nor is it affected by the agency of galvanism. Chemists, indeed, are unable to resolve it into more simple parts, and consequently it is regarded as an elementary principle.

The violet hue of the vapour of iodine is for many purposes a sufficiently sure indication of its presence. A far more delicate test, however, was discovered by Colin and Gaultier de Claubry. They found that iodine has the property of uniting with starch, and of forming with it a compound insoluble in cold water, which is recognised with certainty by its deep blue colour. This test, according to Stromeyer, is so delicate, that a liquid containing 1—450,000ths of its weight of iodine receives a blue tinge from a solution of starch. Two precautions should be observed to insure success. In the first place, the iodine must be in a free state; for it is the iodine itself only, and not its compounds, which unites with starch. Secondly, the solution should be quite cold at the time of adding the starch; for hot water dissolves the blue compound, and forms a colourless solution.

Berzelius determined the equivalent of iodine by exposing fused iodide of silver to a current of chlorine gas, whereby the iodine was expelled and chloride of silver generated. Through the known composition of chloride of silver he inferred that of the iodide, and thence found the eq. of iodine. It is 126·3; eq. vol. = 100; symb. I.

The composition of the compounds of iodine described in this section is as follows :—

	Iodine.	Equiv.	Formula.
Hydriodic Acid	126·3 1 eq. + 1	1 eq. hydrogen	=127·3, $\text{H} + \text{I}$ or HI .
Oxide of Iodine } Iodous Acid }	Composition unknown.		
Iodic Acid	126·3 1 eq. + 40	5 eq. oxygen	=166·3, $\text{I} + 5\text{O}$.
Periodic Acid	126·3 1 eq. + 56	7 eq. do.	=182·3, $\text{I} + 7\text{O}$.
Protochloride of Iodine	126·3 1 eq. + 35·42	1 eq. chlorine	=161·72, $\text{I} + \text{Cl}$.
Terchloride do.	126·3 1 eq. + 106·26	3 eq. do.	=232·56, $\text{I} + 3\text{Cl}$.
Perchloride do.	Composition doubtful.		
Protiodide of Phos.	126·3 1 eq. + 15·7	1 eq. phosph.	=142·0, $\text{P} + \text{I}$.
Sesquiodide do.	378·9 3 eq. + 31·4	2 eq. do.	=410·3, $2\text{P} + 3\text{I}$.
Periodide do.	631·5 5 eq. + 31·4	2 eq. do.	=662·9, $2\text{P} + 5\text{I}$.
Iodide of Sulphur	Composition unknown.		
Iodide of Carbon	Composition unknown.		
Periodide of Carbon	Composition unknown.		
Teriodide of Nitrogen	378·9 3 eq. + 14·15	1 eq. nitrogen	=393·05, $\text{N} + 3\text{I}$.

Hydriodic Acid—Prep.—This compound is formed by the direct union of its elements, when a mixture of hydrogen gas and iodine vapour are transmitted through a porcelain tube at a red heat. A more convenient process, and by which it is obtained in a pure state, is by the action of water on the periodide of phosphorus. Any convenient quantity of the iodide is put into a small glass retort, together with a little water, and a gentle heat is applied. Mutual decomposition ensues; the oxygen of the water unites with phosphorus, and its hydrogen with iodine, giving rise to the formation of phosphoric and hydriodic acids, the latter of which passes over in the form of a colourless gas. The preparation of the iodide requires care; since phosphorus and iodine act so energetically on each other by mere contact, that the phosphorus is generally inflamed, and a great part of the iodine expelled in the form of vapour. This inconvenience is avoided by putting the phosphorus into a tube sealed at one end, about twelve inches long, displacing the air by a current of dry carbonic acid gas, then gradually adding the iodine, and promoting the action towards the close by a gentle heat. The materials should be well dried with bibulous paper, and the iodide preserved in a well-stopped dry vessel; for even atmospheric humidity gives rise to copious white fumes of hydriodic

acid. The proportions usually employed are one part of phosphorus to about twelve of iodine. Another process has been recommended by F. d'Arcet, which consists in evaporating hypophosphorous acid until it begins to yield phosphuretted hydrogen, mixing it with an equal weight of iodine, and applying a gentle heat. Hydriodic acid gas of great purity is then rapidly disengaged; its production depending, as in the former process, on the decomposition of water.

Prop.—Hydriodic acid gas has a very sour taste, reddens vegetable blue colours without destroying them, produces dense white fumes when mixed with atmospheric air, and has an odour similar to that of hydrochloric acid gas. The salts which it forms with alkalis are called *hydriodates*. Like hydrochloric acid gas, it cannot be collected over water; for that liquid dissolves it in large quantity.

It is decomposed by several substances which have a strong affinity for either of its elements. Thus oxygen gas, when heated with it, unites with its hydrogen, and liberates the iodine. Chlorine effects the decomposition instantly; hydrochloric acid gas is produced, and the iodine appears in the form of vapour. With strong nitrous acid it takes fire, and the vapour of iodine is set free. It is also decomposed by mercury. The decomposition begins as soon as hydriodic acid gas comes in contact with mercury, and proceeds steadily, and even quickly if the gas is agitated, till nothing but hydrogen remains. Gay-Lussac ascertained by this method that 100 measures of hydriodic acid gas contain precisely half their volume of hydrogen. Assuming it to consist of equal volumes of hydrogen gas and iodine vapour united without any condensation, then, since

	Grains.
50 cubic inches of the vapour of iodine weigh	134.92
50 do. hydrogen gas	1.0684
100 cubic inches of hydriodic acid gas should weigh	135.9884.

These numbers are obviously in the ratio of 1 to 126.3, the eq. of iodine and hydrogen. On the same principles the density of the gas should be 4.3850, which is probably more correct than 4.443, a number found experimentally by Gay-Lussac (*An. de Ch. xci.* 16). From these coincidences there is no doubt that 100 measures of hydriodic acid gas contain 50 measures of hydrogen gas and 50 of the vapour of iodine.

When the gas is conducted into water till that liquid is fully charged with it, a colourless acid solution is obtained, which emits white fumes on exposure to the air, and has a pungent odour. It may be prepared also, by transmitting a current of hydrosulphuric acid gas through water in which iodine in fine powder is suspended. The iodine, from having a greater affinity than sulphur for hydrogen, decomposes the hydrosulphuric acid; and hence sulphur is set free, and hydriodic acid produced. As soon as the iodine has disappeared and become colourless, it is heated for a short time to expel the excess of hydrosulphuric acid, and subsequently filtered to separate free sulphur.

The solution is readily decomposed. On exposure during a few hours to the atmosphere, the oxygen of the air forms water with the hydrogen of the acid, and sets iodine free. The solution is found to have acquired a yellow tint from the presence of uncombined iodine, and a blue colour is occasioned by the addition of starch. Nitric and sulphuric acid likewise decompose it by yielding oxygen, the former being at the same time converted into nitrous, and the latter into sulphurous acid. Chlorine unites directly with the hydrogen of the hydriodic acid, and hydrochloric acid is formed. The separation of iodine in all these cases may be proved in the way just mentioned. These circumstances afford a sure test of the presence of hydriodic acid, whether free or in combination with alkalies. All that is necessary, is to mix a cold solution of starch with the liquid, previously concentrated by evaporation if necessary, and then add a few drops of strong sulphuric acid. A blue colour will make its appearance if hydriodic acid is present.

Its eq. is 127.3; eq. vol. = 200; symb. H + I, or HI.

Oxide of Iodine and Iodous Acid.—On mixing the vapour of iodine and oxygen gas considerably heated, the violent tint of the former disappears, and a yellow matter of the consistence of solid oil is generated, which Sementini regards as oxide of iodine; and if the supply of oxygen be kept up after its formation, it is converted into a yellow liquid, which he supposes to be iodous acid. From the mode in which the process is described, there can scarcely be a doubt that some compound of iodine and oxygen is thus formed; but its composition and properties have not been satisfactorily made out. (Quarterly Journ. of Science, N. S. i. 478.) On dissolving iodine in a rather dilute solution of soda, until the solution begins to acquire a red tint, permanent crystals are obtained by spontane-

only evaporation, in six-sided prisms, which dissolve in cold water without change, but by the action of water moderately heated, or by alcohol are converted into iodate of soda and iodide of sodium. On the addition of an acid, iodine and iodic acid were set at liberty. From these facts Mitscherlich infers the crystals to be iodite of soda. (Ann. d. Chem. u. Ph. xix. 84.) They are more probably the dihydrate.

Iodic acid.—*Hist. and Prep.*—This acid was discovered at about the same time by Gay-Lussac and Davy; but the latter first succeeded in obtaining it in a state of perfect purity. When iodine is brought into contact with the euchlorine of Davy, immediate action ensues; the chlorine unites with one portion of iodine, and the oxygen with another, forming two compounds, a volatile orange-coloured matter, chloride of iodine, and a white solid substance, which is iodic acid. On applying heat, the former passes off in vapour, and the latter remains (Phil. Trans. for 1815). Serullas has obtained it, in the form of hexagonal laminæ, by evaporating in a warm place its solution either in water, or in sulphuric or nitric acids. The method which he found most convenient is by forming a solution of iodate of soda in a considerable excess of sulphuric acid, keeping it at a boiling temperature for twelve or fifteen minutes, and then setting it aside to crystallize (Ann. de Ch. et Ph. xliii. 316). Iodic acid may also be formed by dissolving perchloride of iodine in water, and gradually adding a large quantity of strong sulphuric acid, a rise of temperature being at the same time prevented by the application of cold. Iodic acid will then be precipitated. The action of strong alcohol on moist perchloride produces the same result: water and the perchloride decomposed, and hydrochloric and iodic acids formed. The latter is left undissolved by the alcohol. Another process, suggested by Mr. Connell of Edinburgh, is by boiling iodine in nitric acid. For this purpose a pure acid of density 1.5 should be introduced with about a fifth of its weight of iodine into a tube sealed at one end, about an inch wide and 15 inches long, and these materials be kept at a boiling temperature for at least twelve hours. As the iodine rises and condenses on the sides of the tube, it should be restored to the liquid, either by agitation or by help of a glass rod. As soon as the iodine disappears, the nitric acid is dissipated by cautious evaporation. It is also obtained, as remarked by Balard, by the oxidizing effect of hypochlorous acid on iodine; the latter unites

with the oxygen of the acid, and the chlorine escapes in the gaseous state.

Prop.—This compound, which was termed *oxiodine* by Davy, is *anhydrous iodic acid*. It is a white semitransparent solid, which has a strong astringent sour taste, but no odour. Its sp. gr. is considerable, as it sinks rapidly in sulphuric acid. When heated to the temperature of about 500° F. it is fused, and at the same time resolved into oxygen and iodine. In a dry air it is unchanged; but in a moist atmosphere it absorbs humidity, forming the *hydrated acid*, and eventually deliquesces. In water it is very soluble, and the solution has a distinct acid reaction: the bleaching power ascribed to it by Davy is said by Hiley not to be a property of pure iodic acid. (Lancet for July 1833.) On evaporating the solution, a thick mass of the consistence of paste is left, which is *hydrous iodic acid*; and which, by the cautious application of heat, may be rendered anhydrous. It acts powerfully on inflammable substances. With charcoal, sulphur, sugar, and similar combustibles, it forms mixtures which detonate when heated. It enters into combination with metallic oxides, and the resulting salts are called *iodates*. These compounds, like the chlorates, yield pure oxygen by heat, and deflagrate when thrown on burning charcoal.

Iodic acid forms with the pure alkalis salts which are soluble in water; but with lime, baryta, strontia, and the oxides of lead and silver, it yields compounds of very sparing solubility. It is readily detected by the facility with which it is deoxidized, an effect readily produced by the sulphurous, phosphorous, hydriodic, and hydro-sulphuric acids. Iodine in each case is set at liberty, and may be detected as usual by starch. Hydrochloric and iodic acids decompose each other, water and chloride of iodine being generated.

Davy ascertained the composition of iodic acid by determining the quantity of oxygen which the acid loses when decomposed by heat; Gay-Lussac arrived at the same result by heating iodate of potassa, when pure oxygen was given and iodide of potassium remained. Its eq. is 166·3; symb. $I + 5O$, $\overset{\cdot\cdot\cdot}{I}$, or IO_5 .

Periodic Acid.—*Hist. and Prep.*—This compound has been lately discovered by Ammermüller and Magnus. (Pogg. Annalen, xxviii. 514.) When pure soda is mixed with a solution of iodate of soda, and chlorine gas is transmitted into it to saturation, a sparingly soluble white pulverulent salt is generated, which sub-

sides after heating, and if necessary, concentrating the solution. This salt is a periodate of soda, the production of which appears to depend on the formation of chloride of sodium, and the union of the oxygen of the soda with the iodine of the iodic acid. For each equivalent of periodic acid, 2 eqs. of chloride of sodium should be generated; since the materials $I + 5O$, $2(Na + O)$, $2Cl$, just suffice for yielding $I + 7O$, and $2(Na + Cl)$. On dissolving the periodate of soda in dilute nitric acid, and adding nitrate of oxide of silver, the periodate of this oxide of a greenish-yellow colour subsides, which should be washed with water acidulated with nitric acid. This yellow salt is soluble in hot dilute nitric acid, and separates again on cooling in small shining straw-yellow crystals, which by digestion with warm water acquire, without dissolving, a reddish-brown almost black colour. If the nitric acid solution of the yellow salt is so far concentrated by evaporation that it crystallizes while still warm, orange-coloured crystals subside. These three salts are readily analyzed by exposure to a red heat in a glass tube, when iodine and metallic silver remain in the tube, and oxygen gas along with water, when water is present, is expelled. Their composition is as follows:—

	Oxide of Silver.	Periodic Acid.	Water.	Formulsæ.
Yellow Salt	232 2 eq.	182·3 1 eq.	27 3 eq.	$(AgO)_2 IO_7 + 3Aq.$
Red Salt	232 2 eq.	182·3 1 eq.	18 2 eq.	$(AgO)_2 IO_7 + 2Aq.$
Orange Salt	116 1 eq.	182·3 1 eq.	0	$AgO, IO_7.$

The two former are therefore hydrated subperiodates of oxide of silver, and the latter a neutral periodate. This neutral salt has the peculiarity, that by pure cold water it is converted into the yellow subsalt, while the water takes up exactly half of its acid without a trace of silver. By this means a pure solution of periodic acid may be obtained.

Prop.—Periodic acid is analogous in composition to perchloric acid, and has decided acid properties. Its solution may be boiled without decomposition, and on evaporation the acid yields crystals, which do not change by exposure to the air. By hydrochloric acid it is reduced to iodic acid with disengagement of chlorine, and the same change will of course be produced by substances which decompose iodic acid. When the heat is increased beyond 212° , (the precise point is not stated,) periodic acid loses oxygen, and iodic acid remains. Thus is periodic more easy of decomposition than iodic acid. Its eq. is 182·3; symb. $I + 7O$, I , or IO_7 .

Chlorides of Iodine.—Chlorine is absorbed at common temperatures by dry iodine with evolution of heat, and a solid compound of iodine and chlorine results, which was discovered both by Davy and Gay-Lussac. The colour of the product is orange-yellow when the iodine is fully saturated with chlorine, but is of a reddish-orange if iodine is in excess. It is converted by heat into an orange coloured liquid, which yields a vapour of the same tint on increase of temperature. It deliquesces in the open air, and dissolves freely in water. Its solution is colourless, very sour to the taste, and reddens vegetable blue colours, but afterwards destroys them. From its acid properties Davy gave it the name of *chloriodic acid*. Gay-Lussac, on the contrary, calls it *chloride of iodine*, conceiving that the acidity of its solution arises from the presence of hydrochloric and iodic acids, which he supposes to be generated by decomposition of water. From the observations of Serullas and Dumas it appears that there exist two compounds of chlorine and iodine, by the different action of which on water the discordant opinions of Davy and Gay-Lussac may be explained.

This subject has lately been examined by Soubeiran. He has distinguished a compound of three eq. of chlorine and one eq. of iodine, but doubts the existence of the perchloride of iodine of Davy and Gay-Lussac (*Journal de Pharmacie*, Feb. 1837). This compound and a protochloride appears, however, to have been previously described by Kane (*Phil. Mag.* x. 430). The protochloride was obtained by passing a current of chlorine gas into water, in which iodine was diffused. A deep reddish yellow solution is formed, which gives off fumes irritating to the eyes and nose, has a peculiar smell of both its constituents, and first reddens and then bleaches litmus paper. The terchloride was obtained by repeatedly distilling the protochloride; it may also be procured by adding to the protochloride a strong solution of corrosive sublimate, which throws down iodine. The perchloride is supposed to contain 5 eq. of chlorine and 1 eq. of iodine, from giving rise, when decomposed by water, to hydrochloric and iodic acids.

Teriodide of Nitrogen.—From the weak affinity that exists between iodine and nitrogen, these substances cannot be made to unite directly. But when iodine is put into a solution of ammonia, the alkali is decomposed; its elements unite with different portions of iodine, and thus cause the formation of hydriodic acid and iodide of nitrogen. The latter subsides in the form of a dark powdery

der, which is characterised, like quadrochloride of nitrogen, by its explosive property. It detonates violently as soon as it is dried; and slight pressure, while moist, produces a similar effect. Heat and light are emitted during the explosion, and iodine and nitrogen are set free. According to the experiments of M. Colin, iodide of nitrogen consists of one eq. of nitrogen and three of iodine.

It is conveniently made, according to Serullas, by saturating alcohol of 0.852 with iodine, adding a large quantity of pure ammonia, and agitating the mixture. On diluting with water, teriodide of nitrogen subsides, which should be washed by repeated affusion of water and decantation. As thus prepared it is very finely divided, and may be pressed under water without detonating; but if, subsequently to its formation, it is put in contact with pure ammonia, it will afterwards detonate with the same facility as that prepared in the usual manner. Water and teriodide of nitrogen mutually decompose each other, giving rise to the formation of hydriodic and iodic acids and ammonia. The change takes place slowly in cold water; but it is completed in a few minutes, and with scarcely any disengagement of nitrogen, when gentle heat is applied. When a little nitric or sulphuric acid is used, ammonia and iodic acid are alone produced. (An. de Ch. et Ph. xlii. 201.)

Its eq. 393.05; symb. $N + 3I$, or NI_3 .

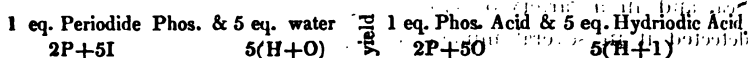
Iodides of Phosphorus.—Iodine and phosphorus combine readily in the cold, evolving so much heat as to kindle the phosphorus, if the experiment is made in the open air; but in close vessels no light appears. One of these compounds, apparently a protiodide, is formed of one part of phosphorus and 7 or 8 parts of iodine. It has an orange colour, fuses at 212° , sublimes unchanged by heat, and is decomposed by water, with the elements of which it gives rise to hydriodic and phosphorous acids, while phosphorus is set free. Its eq. is 142.0; symb. $P + I$, or PI .

The sesquiodide is formed by the action of 1 part of phosphorus and 12 of iodine. It appears as a dark grey crystalline mass, fusible at 84° , and yields with water hydriodic and phosphorous acids, from which circumstance its elements are supposed to be in the ratio of 2 eq. of phosphorus to 3 eq. of iodine.

Its eq. is 410.3; symb. $2P + 3I$, or P_2I_3 .

The periodide is prepared with 1 part of phosphorus and 20 of iodine, and is a black compound, fusible at 114° . As by the action of water it yields hydriodic and phosphoric acids only, it is inferred to

contain phosphorus and iodine in the ratio of 2 eq. to 5 eq. Thus



Its eq. is 662.9; symb. $2P + 5I$, or $P_2 I_5$.

Iodide of Sulphur.—This compound is formed by heating gently 4 parts of iodine with 1 of sulphur. The product has a dark colour and radiated appearance, like antimony. Its elements are easily disunited by heat.

Periodide of Carbon.—When a solution of pure potassa in alcohol is mixed with an alcoholic solution of iodine, a portion of alcohol is decomposed; and its hydrogen and carbon, uniting separately with iodine, give rise to periodide of carbon and hydriodic acid. The latter combines with the potassa, and remains in solution. The former has a yellow colour like sulphur, and forms scaly crystals of a pearly lustre; its taste is very sweet, and it has a strong aromatic odour resembling saffron. It was discovered by Serullas, and described by him as a hydrocarburet of iodine; but its real nature was pointed out by Mitscherlich (An. de Ch. et Ph. xxxvii. 86).

The protiodide is formed by distilling a mixture of the preceding compound with corrosive sublimate. It is a liquid of a sweet taste, and has a penetrating ethereal odour.

SECTION XIV.

BROMINE.

BROMINE was discovered in 1826 by Balard of Montpellier. The name originally applied to it was *muride*, but the term *brome* or *bromine*, from *βρωμος graveolentia*, signifying a strong or rank odour, has since been substituted (An. of Phil. xviii. 381).

Bromine in its chemical relations bears a close analogy to chlorine and iodine, and has hitherto been always found in nature associated with the former, and sometimes also with the latter. It exists in sea-water in the form of bromide of sodium or magnesium. Its relative quantity, however, is very minute; and even the uncrystallizable residue called *bittern*, left after chloride of sodium has been separated from sea-water by crystallization, contains it in small proportion. It may apparently be regarded as an essential ingredient of the saline matter of the ocean; for it has been detected in the waters of the Mediterranean, Baltic, North Sea, and

Firth of Forth. It has also been found in the waters of the Dead Sea, and in a variety of salt springs in Germany. Daubeny has detected it in several mineral springs in England, and states that it is rarely wanting in those springs which contain much common salt, except that of Droitwich in Worcestershire. Balard found that it exists in marine plants growing on the shores of the Mediterranean, and has procured it in appreciable quantity from the ashes of sea-weeds that furnish iodine. He has likewise detected its presence in the ashes of some animals, especially in those of the *Janthina violacea*, one of the testaceous mollusca.

Prep.—Bromine is usually extracted from bittern, and its mode of preparation is founded on the property which chlorine possesses of decomposing hydrobromic acid, uniting with its hydrogen, and setting bromine at liberty. Accordingly, on adding chloride to bittern, the free bromine immediately communicates an orange-yellow tint to the liquid; and on heating the solution to its boiling point, the red vapours of bromine are expelled, and may be condensed by being conducted into a tube surrounded with ice. It was this change of colour produced by chlorine that led to the discovery of bromine. The method recommended by Balard for procuring this substance, as well as for detecting the presence of hydrobromic acid, is to transmit a current of chlorine gas through bittern, and then to agitate a portion of sulphuric ether with the liquid. The ether dissolves the whole of the bromine, from which it receives a beautiful hyacinth-red tint, and on standing it rises to the surface. When the ethereal solution is agitated with caustic potassa, its colour entirely disappears, owing to the formation of bromide of potassium and bromate of potassa, the former of which is obtained in cubic crystals by evaporation. The bromine may then be set free by means of chlorine, or still better by sulphuric acid and the peroxide of manganese. The process should be conducted in a retort, the beak dipping into cold water, which collects the bromine driven over by heat. Balard has subsequently improved the process so much, that it is now produced in considerable quantity, and sold in Paris as an article of commerce.

Prop.—At common temperatures bromine is a liquid, the colour of which is blackish-red when viewed in mass and by reflected light; but appears hyacinth-red when a thin stratum is interposed between the light and the observer. Its odour, which somewhat resembles that of chlorine, is very disagreeable, and its taste powerful. Its sp. gr. is about 3. By a temperature between zero and -4° it is

congealed, and in that state is brittle. Its volatility is considerable; for at common temperatures it emits red-coloured vapours, which are very similar in appearance to those of nitrous acid; and at 116.5° it enters into ebullition. The sp. gr. of its vapours was found by Mitscherlich to be 5.54, and the number calculated (p. 231) from its equivalent is 5.398: 100 cubic inches at 60° and 30 inches B. should weigh 167.25 grains. It is a non-conductor of electricity, and undergoes no chemical change whatever from the agency of the imponderables. It may be transmitted through a red-hot glass tube, and be exposed to the agency of galvanism, without evincing the least trace of decomposition. Like oxygen, chlorine, and iodine, it is a negative electric. It is soluble in water, alcohol, and ether, the latter being its best solvent. It does not redden litmus paper, but bleaches it rapidly like chlorine; and it likewise discharges the blue colour from a solution of indigo. Its vapour extinguishes a lighted taper; but before going out, it burns for a few seconds with a flame which is green at its base and red at its upper part. Some inflammable substances take fire by contact with bromine, in the same manner as when introduced into an atmosphere of chlorine. It acts with energy on organic matters, such as wood or cork, and corrodes the animal texture; but if applied to the skin for a short time only, it communicates a yellow stain, which is less intense than that produced by iodine, and soon disappears. To animal life it is highly destructive, one drop of it placed on the beak of a bird having proved fatal.

From the close resemblance observable between chlorine and bromine, Balard was of course led to examine its relations with hydrogen, and found that these substances may readily be made to unite; the product of the combination being a gas very similar to hydrochloric and hydriodic acid gases, whence it has received the name of *hydrobromic acid gas*. In its action on metals, also, bromine presents the closest similarity to that which chlorine exerts on the same substances. Antimony and tin take fire by contact with bromine; and its union with potassium is attended with such intense heat as to cause a vivid flash of light, and often to burst the vessel in which the experiment is performed. Its affinity for metallic oxides is feeble. By the action of alkalies it is resolved into hydrobromic and bromic acids, suffering the same kind of change as chlorine or iodine when similarly treated.

According to all the experiments hitherto made, bromine ap-

power to be an element. It is so very similar in most aspects to chlorine and iodine, and in the order of its chemical relations is so constantly intermediate between them, that Balard at first supposed it to be some unknown compound of these substances. There is, however, to be no good ground for the supposition; but, still the contrary, an experiment performed by De la Rive affords every strong argument against it. He finds that when a compound of bromine and iodine is mixed with starch, and exposed to the influence of galvanism, bromine appears at the + and iodine at the - wire, where the starch acquires a blue tint. On making the experiment with bromine containing a little bromide of iodine, the same appearance ensues; but if iodine is not previously added, the starch does not receive a tint of blue.

Bromine is in most cases easily detected by means of chlorine; for this substance displaces bromine from its combination with hydrogen, metals, and most other bodies. The appearance of its vapour or the colour of its solution in ether will then render its presence obvious. Like chlorine, it forms a crystalline hydrate when exposed to 32° F. in contact with water. The crystals are octahedral, of a beautiful red tint, and suffer decomposition at 54°. (Lowig.)

Berzelius determined the equivalent of bromine in the same way as that of iodine, namely, by heating a known weight of bromide of silver in a current of chlorine gas, so as to displace the bromine and obtain chloride of silver.

Its eq. is 78·4; eq. vol. = 100; symb Br.

The compounds of bromine described in this section are as follows:—

	Bromine.		Equiv.		Formulae.
Hydrobromic Acid	78·4	1 eq. + Hydrogen	1	1 eq. = 79·4.	H + Br.
Bromic Acid	78·4	1 eq. + Oxygen	40	5 eq. = 118·4.	Br + 5O.
Chloride of Bromine	Composition uncertain.				
Bromides of Iodine	Composition uncertain.				
Bromide of Sulphur	Composition uncertain.				
Protobromide of Phosph.	78·4	1 eq. + phosph.	15·7	1 eq. = 94·1.	P + Br.
Perbromide of Phosph.	392	5 eq. + do.	31·4	2 eq. = 423·4.	2P + 5Br.
Bromide of Carbon	Composition uncertain.				
Terbromide of Silicon	235·2	3 eq. + Silicon	22·5	1 eq. = 257·7.	Si + 3Br.

Hydrobromic Acid.—*Prep.*—No chemical action takes place between the vapour of bromine and hydrogen gas at common temperatures, not even by the agency of the direct solar rays; but on introducing a lighted candle, or a piece of red-hot iron, into the mixture, combination ensues in the vicinity of the heated body,

though without extending to the whole mixture, and without explosion. The combination is readily effected by the action of bromine on some of the gaseous compounds of hydrogen. Thus, on mixing the vapour of bromine with hydriodic acid, hydrosulphuric acid, or phosphuretted hydrogen gases, decomposition ensues, and hydrobromic acid gas is generated. It may be conveniently made for experimental purposes by a process similar to that for forming hydriodic acid. A mixture of bromine and phosphorus, slightly moistened, yields, by the aid of gentle heat, a large quantity of pure hydrobromic acid gas, which should be collected either in dry glass bottles, or over mercury.

Prop.—It is a colourless gas, has an acid taste, and pungent odour. It irritates the glottis powerfully, so as to excite cough, and when mixed with moist air, yields white vapours, which are denser than those occasioned under the same circumstances by hydrochloric acid gas. It undergoes no decomposition when transmitted through a red-hot tube, either alone, or mixed with oxygen. It is not affected by iodine; but chlorine decomposes it instantly, with production of hydrochloric acid gas, and deposition of bromine. It may be preserved without change over mercury; but potassium and tin decompose it with facility, the former at common temperatures, and the latter by the aid of heat. It is very soluble in water. The aqueous solution may be made by treating bromine with hydrosulphuric acid dissolved in water, or still better, by transmitting a current of hydrobromic acid gas into pure water. The liquid becomes hot during the condensation, acquires great density, increases in volume, and emits white fumes when exposed to the air. This acid solution is colourless when pure, but possesses the property of dissolving a large quantity of bromine, and then receives the tint of that substance.

Chlorine decomposes the solution of hydrobromic acid in an instant. Nitric acid likewise acts upon it, though less suddenly, occasioning the disengagement of bromine, and probably the formation of water and nitrous acid. Nitro-hydrobromic acid is analogous to *aqua regia*, and possesses the property of dissolving gold. The elements of sulphuric and hydrobromic acids react on each other in a slight degree; and hence, on decomposing bromide of potassium by sulphuric acid, the hydrobromic is generally mixed with a little sulphurous acid gas.

The composition of hydrobromic acid gas is easily inferred from

the two following facts. 1. On decomposing hydrobromic acid gas by potassium, a quantity of hydrogen remains, precisely equal to half the volume of the gas employed; and, 2, when hydriodic acid gas is decomposed by bromine, the resulting hydrobromic acid occupies the very same space as the gas which is decomposed. Hence hydrobromic is analogous to hydriodic and hydrochloric acid gases, in containing equal measures of bromine vapour and hydrogen gas united without any change of volume; and since

		Grains.
50 cubic inches of Bromine vapour weigh	. . .	83·64
50 do. Hydrogen gas	. . .	1·0684
100 do. Hydrobromic acid must weigh	. . .	84·7084

These numbers are in the ratio of 1 to 78·4, which is the composition of the gas by weight. Its sp. gr. is 2·731.

Since bromine decomposes hydriodic, and chlorine hydrobromic acid, bromine, in relation to hydrogen, is intermediate between chlorine and iodine; for it has a stronger affinity for hydrogen than iodine, and a weaker than chlorine. The affinity of bromine and oxygen for hydrogen appears nearly similar; for while oxygen cannot detach hydrogen from bromine, bromine does not decompose watery vapour.

The salts of hydrobromic acid are termed *hydrobromates*. Like the free acid, they are decomposed, and the presence of bromine is detected, by means of chlorine. On mixing a soluble bromide with the nitrates of the protoxides of lead, silver, and mercury, white precipitates are obtained, which are very similar in appearance to the chlorides of those metals, but which are metallic bromides. On the addition of chlorine, the vapour of bromine is evolved.

Its eq. is 79·4; eq. vol. = 200; symb. H + Br, or H Br.

Bromic Acid.—*Prep.*—The only compound yet known of bromine and oxygen is that formed by the action of bromine on potassa, when a change exactly similar to that produced by chlorine (page 343) ensues, whereby bromide of potassium and bromate of potassa are generated; and the latter, being much less soluble than the former, is readily separated by evaporation. The bromate of the other alkalies and alkaline earths may be prepared in a similar manner.

The acid may be procured in a separate state by decomposing a dilute solution of bromate of baryta with sulphuric acid, so as to precipitate the whole of the baryta. The resulting solution of

bromic acid may be concentrated by slow evaporation until it acquire the consistence of syrup; but on raising the temperature, in order to expel all the water, one part of the acid is volatilized, and the other resolved into oxygen and bromine. A similar result took place when the evaporation was conducted *in vacuo* with sulphuric acid; and accordingly all attempts to procure anhydrous bromic acid have hitherto failed.

Prop.—Bromic acid has scarcely any odour, but its taste is very acid, though not at all corrosive. It reddens litmus paper powerfully at first, and soon after destroys its colour. It is not affected by nitric or sulphuric acids except when the latter is highly concentrated, in which case bromine is set free, and effervescence, probably owing to the escape of oxygen gas, ensues. From the analysis of bromate of potassa, bromic acid is obviously similar in constitution to iodic, chloric, and nitric acids; that is, it consists of one equivalent of bromine united with five of oxygen. Its salts are analogous to the chlorates and iodates. Thus bromate of potassa is converted by heat into bromide of potassium, with disengagement of pure oxygen gas, deflagrates like nitre when thrown on burning charcoal, and forms with sulphur a mixture which detonates by percussion. The acid of the bromates is decomposed by deoxidizing agents, such as sulphurous and hydrosulphuric acids, in the same manner as the acid of the iodates. The bromates likewise suffer decomposition from the action of hydrobromic and hydrochloric acids.

Bromate of potassa is said not to precipitate the salts of lead, but to occasion a white precipitate with nitrate of silver, and a yellowish-white with protonitrate of mercury; characters which, if true, serve as a good test to distinguish bromate from iodate and chlorate of potassa.

Its eq. is 118.4; symb. $\text{Br} + 5\text{O}$, $\ddot{\text{Br}}$, or BrO_5 .

Chloride of Bromine.—This compound may be formed at common temperatures by transmitting a current of chlorine through bromine, and condensing the disengaged vapours by means of a freezing mixture. The resulting chloride is a volatile fluid of a reddish-yellow colour, much less intense than that of bromine; its odour is penetrating, and causes a discharge of tears from the eyes; and its taste very disagreeable. Its vapour is a deep yellow, like chlorous acid, and it enables metals to burn as in an atmosphere of chlorine, doubtless giving rise to the formation of metallic chlorides and bromides.

Chloride of bromine is soluble in water without decomposition ; for the solution possesses the colour, odour, and bleaching properties of the compound, and discharges the colour of litmus paper without previously reddening it. By the action of the alkalies it is decomposed, being converted, by means of the elements of water, into hydrochloric and bromic acids.

Bromine of Iodine.—These substances act readily on each other, and appear capable of uniting in two proportions. The protobromide is a solid, convertible by heat into a reddish-brown vapour, which, in cooling, condenses into crystals of the same colour, and of a form resembling that of fern leaves. An additional quantity of bromine converts these crystals into a fluid, which in appearance is like a strong solution of iodine in hydriodic acid. This compound dissolves without decomposition in water, but with the alkalies yields hydrobromic and iodic acids. The existence of two bromides of iodine can scarcely be regarded as satisfactorily established.

Bromide of Sulphur.—On pouring bromine on sublimed sulphur, combination ensues, and a fluid of an oily appearance and reddish tint is generated. In odour it somewhat resembles chloride of sulphur, and like that compound emits white vapours when exposed to the air ; but its colour is deeper. It reddens litmus paper faintly when dry, but strongly if water is added. Cold water acts slowly upon bromide of sulphur ; but at a boiling temperature the action is so violent that a slight detonation occurs, and three compounds, hydrobromic, hydrosulphuric, and sulphuric acids are formed. The formation of these substances is of course attributable to decomposition of water, and the union of its elements with bromine and sulphur. Bromide of sulphur is likewise decomposed by chlorine, which unites with sulphur, and displaces bromine.

The composition of bromide of sulphur is unknown. It dissolves an excess both of chlorine and sulphur, and its elements separate from each other so readily, that it has hitherto been impracticable to procure a definite compound.

Bromide of Phosphorus.—When bromine and phosphorus are brought into contact in a flask filled with carbonic acid gas, they act suddenly on each other with evolution of heat and light, and two compounds are generated : one, a crystalline solid, which is sublimed and collects in the upper part of the flask ; and the other,

a fluid, which remains at the bottom. The former contains the most bromine, and the latter is supposed by Balard to consist of single equivalents of its elements.

The protobromide retains its liquid form even at 52° F. It is readily converted into vapour by heat, and on exposure to the air emits penetrating fumes. It reddens litmus paper faintly, an effect which is probably owing to the presence of moisture. With water it acts energetically and with free disengagement of heat, hydrobromic acid gas being evolved when only a few drops of water are employed; but if a large quantity is used, the gas is dissolved, and the acid solution leaves by evaporation a residuum, which burns slightly when dried, and is converted into phosphoric acid.

The perbromide is yellow in its solid state; but with gentle heat it becomes a red-coloured liquid, which by increase of temperature is converted into a vapour of the same tint. On cooling after fusion it yields rhombic crystals; but when its vapour is condensed, the crystals are acicular. It is decomposed by metals, probably with the formation of metallic bromides and phosphurets. It emits dense penetrating fumes on exposure to the air, and with water gives rise to the production of hydrobromic and phosphoric acids. Hence its elements should be in the ratio of 2 eqs. of phosphorus to 5 eqs. of bromine.

Chlorine has a greater affinity for phosphorus than bromine, and decomposes both the bromides with evolution of the vapour of bromine. These compounds are not decomposed by iodine; but, on the contrary, bromine decomposes iodide of phosphorus.

Bromide of Carbon.—This compound is formed by the action of bromine on half its weight of periodide of carbon, when bromide of carbon and a sub-bromide of iodine are formed, the latter of which is removed by a solution of caustic potassa. At common temperatures it is liquid, but crystallizes at 32° F. Its taste is sweet, and it has a penetrating ethereal odour. It resembles protiodide of carbon in many respects, but is distinguished from it by the vapour which it emits on exposure to heat (Serullas, An. de Ch. et Ph. xxxix. 225).

Terbromide of Silicon.—This compound was made by Serullas in precisely the same mode as that described for forming the terchloride. When purified from free bromine by mercury, and redistilled, it is a colourless liquid, which emits dense vapours in an open vessel, being decomposed by the moisture of the air, and is

denser than strong sulphuric acid. At 302° it enters into ebullition, and freezes at 10° . Potassium, when gently heated, acts on it with such energy that detonation ensues. By water it is resolved into hydrobromic and silicic acids. (Phil. Mag. and Annals, xi. 295.) Its eq. is 257.7; symb. $\text{Si} + 3\text{Br}$, or Si Br_3 .

SECTION XV.

FLUORINE.

THE substance to which this name is applied, though long known to exist in various compounds, has only recently been obtained in an insulated form, and therefore the properties peculiar to it in that state are but imperfectly known. It was first procured by Baudrimont by passing fluoride of boron over minium heated to redness, and receiving the gas in a dry vessel. As it is mixed with a large quantity of oxygen, his present method is to treat a mixture of fluoride of lime and peroxide of manganese with strong sulphuric acid. This process, however, does not give a pure gas, as hydrofluoric and fluosilicic acid gases are at the same time evolved. The presence of the latter do not prevent the observation of some of the properties of fluorine. It is a gas of a yellowish-brown colour; its odour resembles chlorine and burnt sugar; it bleaches. It does not act on glass, but combines directly with gold (Phil. Mag. x. 149). The latter fact is confirmed by the observations of Messrs. Knox, who have succeeded so far in the preparation of fluorine as to leave no doubt of its existence as a coloured gas (Phil. Mag. x. 107). Its sp. gr. is 1.289. From the nature of its compounds it appears to belong to the class of negative electrics, and, like oxygen and chlorine, to have a powerful affinity for hydrogen and metallic substances. Berzelius determined its eq. by finding that 100 parts of pure fluoride of calcium yield with sulphuric acid 175 parts of sulphate of lime. Its eq. is 18.68; eq. vol. = 100; symb. F.

The compounds of fluorine described in this section are the following:—

	Fluorine.		Equiv. Formulæ.
Hydrofluoric acid	18.68 1 eq. + Hydrogen	1.	1 eq. = 19.68. $\text{H} + \text{F}$.
Fluoboric acid	56.08 3 eq. + Boron	10.9	1 eq. = 66.98. $\text{B} + 3\text{F}$.
Fluosilicic acid	56.08 3 eq. + Silicon	22.5	1 eq. = 78.58.

Hydrofluoric Acid.—*Hist. and Prep.*—This acid was first procured in its pure state in the year 1810 by Gay-Lussac and

Thenard, and described in the second volume of their *Recherches Physico-Chimiques*. It is prepared by acting on the mineral called *fluorspar*, which is a fluoride of calcium, carefully separated from siliceous earth and reduced to fine powder, with twice its weight of concentrated sulphuric acid. The mixture is made in a leaden retort; and on applying heat, an acid and highly corrosive vapour distils over, which must be collected in a receiver of the same metal surrounded with ice. As the materials swell up considerably during the process, owing to a quantity of vapour forcing its way through a viscid mass, the retort should be capacious. At the close of the operation pure hydrofluoric acid is found in the receiver, and the retort contains dry sulphate of lime. The chemical changes are precisely the same as in the formation of hydrochloric acid gas at page 334, fluorine being substituted for chlorine and calcium for sodium. If the oil of vitriol is of sufficient strength, all its water is decomposed, and the resulting hydrofluoric acid is anhydrous.

Prop.—It is at 32° a colourless fluid, and remains in that state at 59° if preserved in well-stopped bottles; but when exposed to the air, it flies off in dense white fumes, which consist of the acid vapour combined with the moisture of the atmosphere. Its sp. gr. is 1.0609; but its density may be increased to 1.25 by gradual additions of water. Its affinity for this liquid far exceeds that of the strongest sulphuric acid, and the combination is accompanied with a hissing noise, as when red-hot iron is quenched by immersion in water.

Its vapour is much more pungent than chlorine or any of the irritating gases. Of all known substances, it is the most destructive to animal matter. When a drop of the concentrated acid of the size of a pin's head comes in contact with the skin, instantaneous disorganization ensues, and deep ulceration of a malignant character is produced. On this account the greatest care is requisite in its preparation. It acts energetically on glass. The transparency of the glass is instantly destroyed, heat is evolved, and the acid boils, and in a short time entirely disappears. A colourless gas, commonly known by the name of *fluo-silicic acid gas*, is the sole product. This compound is always formed when hydrofluoric acid comes in contact with a siliceous substance. For this reason it cannot be preserved in glass; but must be prepared and kept in metallic vessels. Those of lead, from their cheapness, are often

used; but vessels of silver or platinum are preferable. In consequence of its powerful affinity for siliceous matter, hydrofluoric acid may be employed for etching on glass; and when used with this intention, it should be diluted with three or four times its weight of water.

Hydrofluoric acid has all the usual characters of a powerful acid. It has a strong sour taste, reddens litmus paper, and neutralizes alkalies, either forming salts termed *hydrofluates*, or most generally giving rise to metallic fluorides. All these compounds are decomposed by strong sulphuric acid with the aid of heat, and the hydrofluoric acid while escaping may be detected by its action on glass.

On some of the metals it acts violently, especially on the bases of the alkalies. Thus when potassium is brought in contact with the concentrated acid, an explosion attended with heat and light ensues; hydrogen gas is disengaged, and a white compound, fluoride of potassium, is generated. It is a solvent for some elementary principles which resist the action even of nitro-hydrochloric acid. Thus it dissolves silicon, zirconium, and columbium, with evolution of hydrogen gas; and when mixed with nitric acid, it proves a solvent for silicon which has been condensed by heat, and for titanium. Nitro-hydrofluoric acid, however, is incapable of dissolving gold and platinum. Several oxidized bodies, which are not attacked by sulphuric, nitric, or hydrochloric acid, are readily dissolved by hydrofluoric acid. As examples of this fact, several of the weaker acids, such as silica or silicic acid, titanous, columbic, molybdic, and tungstic acids may be enumerated. (Berzelius.)

A different view of the compounds of fluorine was originally taken by Gay-Lussac and Thenard, and is still held by some chemists. They adopted the opinion that hydrofluoric acid is a compound of a certain inflammable principle and oxygen, and applied to it the name of *fluoric acid*, previously introduced by Scheele. Fluor-spar on this view is a fluuate of lime, and when this salt is decomposed by oil of vitriol, the fluoric is merely displaced by the sulphuric acid, and the former passes off combined with the water of the latter. What I have described as anhydrous hydrofluoric acid is, according to this hypothesis, hydrated fluoric acid; and when acted upon by potassium, this metal is oxidized at the expense of the water, and potassa thus generated unites with fluoric acid, forming, not fluoride of potassium, but fluuate of potassa. The equivalent of fluoric acid, as inferred from the analysis of Ber-

zelius, is 10·68; for 39·18 parts or one equivalent of fluor-spar is supposed to contain 28·5 parts of lime (20·5 calcium and 8 oxygen), thus leaving 10·68 as the equivalent of the acid.

The theory, according to which fluor-spar is a compound of fluorine and calcium, originated as a suggestion with M. Ampère of Paris, and was afterwards supported experimentally by Davy. It was found that pure hydrofluoric acid evinces no sign of containing either oxygen or water. Charcoal may be intensely heated in the vapour of the acid without the production of carbonic acid. When hydrofluoric acid was neutralized with dry ammoniacal gas, a white salt resulted, from which no water could be separated; and on treating this salt with potassium, no evidence could be obtained of the presence of oxygen. On exposing the acid to the agency of galvanism, there was a disengagement at the negative pole of a small quantity of gas, which from its combustibility was inferred to be hydrogen; while the platinum wire of the opposite side of the battery was rapidly corroded, and became covered with a chocolate coloured powder. Davy explained these phenomena by supposing that hydrofluoric acid was resolved into its elements; and that fluorine, at the moment of arriving at the positive side of the battery, entered into combination with the platinum wire which was employed as a conductor. Unfortunately, however, he did not succeed in obtaining fluorine in an insulated state. Indeed, from the noxious vapours that arose during the experiment, it was impossible to watch its progress, and examine the different products with that precision which is essential to the success of minute chemical inquiries, and which Davy has so frequently displayed on other occasions.

Though these researches led to no conclusive result, they afforded so strong a presumption in favour of the opinion of Ampère and Davy, that it was adopted by several other chemists. This view has received strong additional support from the experiments of M. Kuhlman. (*Quarterly Journal of Science* for July 1827, p. 205.) It was found by this chemist that fluor-spar is not in the slightest degree decomposed by the action of anhydrous sulphuric acid, whether at common temperatures or at a red heat. The experiment was made both by transmitting the vapour of anhydrous sulphuric acid over fluor-spar heated to redness in a tube of platinum, and by putting the mineral into the liquid acid. In neither case did decomposition ensue; but when the former experiment

was repeated with the difference of employing concentrated hydrous instead of anhydrous sulphuric acid, evolution of hydrofluoric acid was produced. M. Kuhlman also transmitted hydrochloric acid gas over fluor-spar at a red heat, when hydrofluoric acid was disengaged, without any evolution of hydrogen, and chloride of calcium remained. I am aware of no satisfactory explanation of these facts, except by regarding fluor-spar as a compound of fluorine and calcium, and hydrofluoric acid as a compound of fluorine and hydrogen. I shall accordingly adopt this view in the subsequent pages, and never employ the term fluoric acid except when explaining phenomena according to the theory of Gay-Lussac.

Its eq. is 19.68; symb. $H + F$, or HF .

Fluoboric Acid.—Prep.—The chief difficulty in determining the nature of hydrofluoric acid arises from the water of the sulphuric acid which is employed in its preparation. To avoid this source of uncertainty, Gay-Lussac and Thenard made a mixture of vitrified boracic acid and fluor-spar, and exposed it in a leaden retort to heat, under the expectation that as no water was present, anhydrous fluoric acid would be obtained. In this, however, they were disappointed; but a new gas came over, to which they applied the term of *fluoboric acid gas*. A similar train of reasoning led Davy about the same time to the same discovery; though the French chemists had the advantage in priority of publication. Another process, given by Dr. Davy, is to mix 1 part of vitrified boracic acid and 2 of fluor-spar with 12 parts of strong sulphuric acid, heating the mixture gently in a glass flask (Phil. Trans. 1812); but the gas thus developed contains a considerable quantity of fluosilicic acid. Fluoboric acid gas may also be formed by heating a strong solution of hydrofluoric and boracic acids in a metallic retort.

In the decomposition of fluor-spar by vitrified boracic acid, the former and part of the latter undergo an interchange of elements. The fluorine uniting with boron gives rise to fluoboric acid gas; and by the union of calcium and oxygen lime is generated, which combines with boracic acid, and is left in the retort as borate of lime. Fluoboric acid gas, therefore, is composed of boron and fluorine. Those who adopt the theory of Gay-Lussac give a different explanation, and regard this gas as a compound of fluoric and boracic acids. The lime of fluor-spar is supposed to unite with one portion of boracic acid, and fluoric acid at the moment of separation with another, yielding borate of lime and fluoboric acid gas.

Prop.—It is colourless gas, has a penetrating pungent odour, and extinguishes flame on the instant. Its sp. gr. according to Thomson, is 2.3622. It reddens litmus paper as powerfully as sulphuric acid, and forms salts with alkalies which are called *fluoborates*. It has a singularly great affinity for water. When mixed with air or any gas which contains watery vapour, a dense white cloud, a combination of water and fluoboric acid, appears, thus affording an extremely delicate test of the presence of moisture in gases. Water acts powerfully on this gas, absorbing, according to Dr. Davy, 700 times its volume, during which the water increases in temperature and volume. The solution is limpid, fuming, and very caustic. On the application of heat, part of the gas is disengaged; but afterwards the whole solution is distilled.

Gay-Lussac and Thenard and Dr. Davy were of opinion that fluoboric acid gas is dissolved by water without decomposition; but Berzelius denies the accuracy of their observation. On transmitting the gas into water until the liquid acquires a sharply sour taste, but is far from being saturated, a white powder begins to subside; and, on cooling, a considerable quantity of boracic acid is deposited in crystals. It appears that in a certain state of dilution, part of the fluoboric acid and water mutually decompose each other, with formation of boracic and hydrofluoric acids. The latter unites, according to Berzelius, with undecomposed fluoboric acid, forming what he has called *boro-hydrofluoric acid*. On concentrating the liquid by evaporation, the boracic and hydrofluoric acids decompose each other, and the original compound is re-produced.

Fluoboric acid gas does not act on glass, but attacks animal and vegetable matters with energy, converting them like sulphuric acid into a carbonaceous substance. This action is most probably owing to its affinity for water.

When potassium is heated in fluoboric acid gas, the metal takes fire, and a chocolate-coloured solid, wholly devoid of metallic lustre, is formed. This substance is a mixture of boron and fluoride of potassium, from which the latter is dissolved by water, and the boron is left in a solid state.

The composition of fluoboric acid gas has not hitherto been determined by direct experiment. Dr. Davy ascertained that it unites with an equal measure of ammoniacal gas, forming a solid salt; and that it also combines with twice and three times its volume of ammonia, yielding liquid compounds. In the former salt the relative

weights of the constituent gases are in the ratio of their specific gravities; and if the compound consists of one equivalent of each, it will be constituted of,

Fluoboric acid gas	.	.	2.3622	.	68.04	one eq.
Ammoniacal gas	.	.	0.6898	.	17	one eq.

so that the equivalent of the acid may be assumed in round numbers to be 68. Now supposing this acid to be formed of three eqs. of fluorine and one of boron, its eq. will be 64.04, a number which approximates to the preceding. This view is consistent with the composition of boracic as given at page 321, and with the conversion of fluoboric acid by water into hydrofluoric and boracic acids.

Its symb. is $B + 3F$, or BF_3 .

Fluosilicic Acid.—*Prep.*—This gas is formed whenever hydrofluoric and silicic acids come in contact; and hence pure hydrofluoric acid can be prepared in metallic vessels only, and with fluor spar that is free from rock crystal. The most convenient method of procuring it, is to mix in a retort one part of pulverized fluor spar with its own weight of sand or pounded glass, and two parts of strong sulphuric acid. On applying a gentle heat, fluosilicic acid gas is disengaged with effervescence, and may be collected over mercury.

The chemical changes attending this process are differently explained, according to the view which is taken concerning the nature of the product. In regarding fluor spar as a compound of fluoric acid and lime, the former at the moment of being set free is thought to unite directly with silicic acid, thereby giving rise to a compound of silicic and fluoric acids. But for reasons already stated (page 378), fluor-spar is not considered as fluuate of lime; and therefore this view cannot be admitted. It is inferred, on the contrary, that when, by the action of sulphuric acid on fluoride of calcium, hydrofluoric acid is generated, the elements of this acid react on those of silicic acid, and give rise to the production of water and fluosilicic acid gas. This gas is therefore a fluoride of silicon. It may occur to some whether hydrofluoric acid does not unite directly with silicic acid; but this idea is inconsistent with the proportion in which the elements of the gas are found to be united.

Prop.—It is a colourless gas which extinguishes flame, destroys animals that are immersed in it, and irritates the respiratory organs powerfully. It does not corrode glass vessels provided they are quite dry. When mixed with atmospheric air it forms a white cloud, owing to the presence of watery vapour. Its sp. gr. accord-

ing to Thomson, is 3.6111; and 100 cubic inches of it at 60°, and when the barometer stands at 30 inches, weigh 111.985 grains.

Water acts powerfully on fluosilicic acid gas, of which it condenses, according to Dr. Davy, 365 times its volume (Phil. Trans. for 1812). The gas suffers decomposition at the moment of contact with water, silicic acid in the form of a gelatinous hydrate being deposited, which when well washed is quite pure. The liquid, which has a sour taste and reddens litmus paper, contains the whole of the hydrofluoric acid, together with two-thirds of the silicic acid which was originally present in the gas. (Berzelius.) By conducting fluosilicic acid gas into a solution of ammonia, complete decomposition ensues:—hydrofluoric acid unites with the alkali, forming hydrofluat of ammonia, and all the silicic acid is deposited. On this fact is founded the mode of analyzing fluosilicic acid gas, adopted by Dr. Davy and Thomson.

The solution which is formed by fully saturating water with fluosilicic acid gas is powerfully acid, and emits fumes on exposure to the air. It is commonly known by the name of *silicated fluoric acid*; but a more appropriate term is *silico-hydrofluoric acid*. According to the experiments of Berzelius, it appears to be a definite compound of hydrofluoric and silicic acids in the ratio of 3 eqs. of the former to two of the latter. If evaporated before separation from the silicic acid deposited by the action of water on fluosilicic acid gas, this compound is reproduced. But if the solution is poured off from the silicic acid thus deposited, and then evaporated, fluosilicic acid gas is at first evolved, and subsequently hydrofluoric acid and water are expelled. The evaporation of silico-hydrofluoric acid *in vacuo* is attended by a similar change, so that this acid cannot be obtained free from water. It does not corrode glass; but when evaporated in glass vessels, the production of free hydrofluoric acid of course gives rise to corrosion.

On neutralizing silico-hydrofluoric acid with ammonia, and gently evaporating to dryness, all the silicic acid is rendered insoluble. By exactly neutralizing with carbonate of potassa, a sparingly soluble double fluoride of silicon and potassium subsides; the precipitation is still more complete with chloride of barium, when the insoluble fluoride of silicon and barium is generated. A variety of similar compounds may be obtained either by double decomposition, or by the action of silico-hydrofluoric acid on metallic oxides.

Its eq. is 78.58; symb. $\text{Si} + 3\text{F}$, or SiF_3 .

ON THE COMPOUNDS OF THE SIMPLE NON-METALLIC
ACIDIFIABLE COMBUSTIBLES WITH EACH OTHER.

SECTION I.

HYDROGEN AND NITROGEN.—AMMONIACAL GAS.

Hist. and Prep.—THE aqueous solution of ammonia, under the name of *spirit of hartshorn*, has been long known to chemists; but its existence as a gas was first noticed by Priestley, who described it in his works under the title of *alkaline air*. It is often called the *volatile alkali*; but the terms ammonia and ammoniacal gas are now usually employed.

An abundant supply of ammoniacal gas may be obtained from any salt of ammonia by the action of a pure alkali or alkaline earth; but hydrochlorate of ammonia and lime, from economical considerations, are always employed. The proportions to which I give the preference are equal parts of hydrochlorate of ammonia and well-burned quicklime, considerable excess of lime being taken, in order to decompose the hydrochlorate more expeditiously and completely. The lime is slaked by the addition of water; and as soon as it has fallen into powder, it should be placed in an earthen pan and be covered till it is quite cold, in order to protect it from the carbonic acid of the air. It is then mixed in a mortar with the hydrochlorate of ammonia, previously reduced to a fine powder; and the mixture is put into a retort or other convenient glass vessel. Heat is then applied, and the temperature gradually increased as long as free evolution of gas continues. The ammonia should be conducted by means of a safety tube of Welter into a quantity of distilled water equal to the weight of the salt employed. The residue consists of chloride of calcium and lime.

The gas, thus liberated, must be collected over mercury, as it is most rapidly absorbed by water. Advantage is taken of this property to prepare what is commonly though incorrectly termed liquid ammonia. For this purpose a current of gas is transmitted into distilled water, which is kept cool by means of ice or moist cloths, and the process is continued as long as any gas is absorbed. A highly concentrated solution of ammonia is thus obtained. The

most convenient method of preparing ammoniacal gas for purposes of experiment is by applying a gentle heat to the concentrated solution, contained in a glass vessel. It most commonly contains sulphuric acid, and a large quantity of pure ammonia is evolved.

Prop.—Ammonia is a colourless gas, which has a strong pungent odour, and acts powerfully on the eyes and nose. It is quite irrespirable in its pure form, but when diluted with air, it may be breathed into the lungs with safety. Burning bodies are extinguished by it, and the gas is inflamed by their approach. Ammonia, however, is not flammable in a low degree; for when a lighted candle is introduced in it, the flame is somewhat enlarged, and tinged with a pale yellow colour at the moment of being extinguished; and a small jet of the gas will burn in an atmosphere of oxygen. A mixture of ammoniacal and oxygen gases detonates by the electric spark, water being formed, and nitrogen set free. A little nitric acid is generated at the same time, except when a smaller quantity of oxygen is employed than is sufficient for combining with all the hydrogen of the ammonia. (Henry, Phil. Trans. 1809.)

Ammoniacal gas at the temperature of 50° and under a pressure equal to 6.5 atmospheres, becomes a transparent colourless liquid. It is also liquefied, according to Guyton-Morveau, under the common pressure, by a cold of -70° ; but there is no doubt that the liquid which he obtained was a solution of ammonia in water.

It has all the properties of an alkali in a very marked manner. Thus it has an acrid taste, and gives a brown stain to turmeric paper; though the yellow colour soon reappears on exposure to the air, owing to the volatility of the alkali. It combines also with acids, and neutralizes their properties completely. All these salts, suffer decomposition by being heated with the fixed alkalis, or alkaline earths, such as potassa or lime, the union of which with the acid of the salt causes the separation of its ammonia. None of the ammoniacal salts can sustain a red heat without being dissipated in vapour or decomposed, a character which manifestly arises from the volatile nature of the alkali. If combined with a volatile acid, such as the hydrochloric, the compound itself sublimes unchanged by heat; but when united with an acid, which is fixed at a low red heat, such as the phosphoric, the ammonia alone is expelled. It is here considered that the salts of ammonia are formed, by its direct union with acids. Another, and a very scientific view, has been adopted by Berzelius. When an electric current is passed

through a weak solution of ammonia, it is decomposed by the secondary action, hydrogen from decomposed water being evolved at the negative electrode and nitrogen at the positive (Faraday, Phil. Trans. 1834). But if a portion of mercury form the negative electrode, no hydrogen is evolved, and the mercury is rapidly converted into a light porous substance, which has the lustre and all the characters of an amalgam. As soon as it is removed from the influence of the electric current, rapid decomposition ensues, mercury is reproduced, and hydrogen and ammoniacal gases are evolved in the ratio of one measure of the former to two of the latter, according to the observations of Gay-Lussac and Thenard. The production of this compound is explained by Berzelius on the supposition that ammonia by uniting with an additional eq. of hydrogen forms a compound, which has all the properties of a metal; he therefore calls it ammonium. The oxide of ammonium, the composition of which is represented by the formula $\text{NH}_4 + \text{O}$, he considers to be the base of the ammoniacal salts. This view is supported by several facts, which will be considered when treating of the salts.

Hydrogen and nitrogen gases do not unite directly, and therefore chemists have no synthetic proof of the constitution of ammonia. Its composition, however, has been determined analytically with great exactness. When a succession of electric sparks is passed through ammoniacal gas, it is resolved into its elements; and the same effect is produced by conducting it through porcelain tubes heated to redness. A. Berthollet analyzed ammonia in both ways, and ascertained that 200 measures of that gas, on being decomposed, occupy the space of 400 measures, 300 of which are hydrogen, and 100 nitrogen. Henry has made an analysis of ammonia by means of electricity, and his experiment proves beyond a doubt that the proportions above given are rigidly exact. (*Annals of Philosophy*, xxiv. 346.)

		Grains.
Now since 150 cubic inches of hydrogen weigh	.	3.205
and 50 of nitrogen	.	15.083
100 cubic inches of ammonia must weigh	.	18.288

and it is composed by weight of

Hydrogen	.	3.205	.	3	.	or 3 equivalents.
Nitrogen	.	15.083	.	14.15	.	or 1 equivalent.

The sp. gr. of ammonia, according to this calculation, is 0.5898,
2 c

a number which agrees closely with those ascertained directly by Davy and Thomson.

Ammoniacal gas has a powerful affinity for water. Owing to this attraction, a piece of ice, when introduced into a jar full of ammonia, is instantly liquefied, and the gas disappears in the course of a few seconds. Davy, in his *Elements*, stated that water at 50°, and when the barometer stands at 29·8 inches, absorbs 670 times its volume of ammonia, and that the solution has a sp. gr. of 0·875. According to Thomson, water at the common temperature and pressure takes up 780 times its bulk. By strong compression, water absorbs the gas in still greater quantity. Heat is evolved during its absorption; and a considerable expansion, independently of the increased temperature, occurs at the same time.

The concentrated solution of ammonia is a clear colourless liquid, of sp. gr. 0·936. It possesses the peculiar pungent odour, taste, alkalinity, and other properties of the gas itself. On account of its great volatility it should be preserved in well-stopped bottles, a measure which is also required to prevent the absorption of carbonic acid. At a temperature of 130° it enters into ebullition, owing to the rapid escape of pure ammonia; but the whole of the gas cannot be expelled by this means, as at last the solution itself evaporates. It freezes at about the same temperature as mercury.

The following table, from Davy's *Elements of Chemical Philosophy*, shows the quantity of real ammonia contained in 100 parts of solutions of different sp. gravities at 59° F. and when the barometer stands at 30 inches. The sp. gr. of water is supposed to be 10,000:—

Table of the quantity of real Ammonia in solutions of different densities.

100 parts of sp. gravity.		Of real Ammonia.	100 parts of sp. gravity.		Of real Ammonia.
8750	contain	32·5	9435	contain	14·53
8875		29·25	9476		13·46
9000		26·00	9513		12·40
9054		25·37	9545		11·56
9166		22·07	9573		10·82
9255		19·54	9597		10·17
9326		17·52	9619		9·60
9385		15·88	9692		9·50

The presence of free ammoniacal gas may always be detected by its odour, by its temporary action on yellow turmeric paper, and by

its forming dense white fumes, hydrochlorate of ammonia, when a glass rod moistened with hydrochloric acid is brought near it.

Its eq. is 17.15; eq. vol. = 200; symb. $N + 3H$, or NH_3 .

SECTION II.

COMPOUNDS OF HYDROGEN AND CARBON.

CHEMISTS have for several years been acquainted with two distinct compounds of carbon and hydrogen, viz. carburetted hydrogen and olefiant gases; but late researches have enriched the science with several other compounds of a similar nature, to which much interest is attached. They are remarkable for their number, for supplying some instructive instances of isomerism, and for their tendency to unite with and even neutralize powerful acids, without, in their uncombined state, manifesting any ordinary signs of alkalinity. Several of them are particularly distinguished by their chemical affinities; for although compound, they exhibit in their combinations with other substances the characteristics of an element. They have hence been called the compound radicals. These compound radicals are closely associated both with the organic and inorganic chemistry. In the latter they must hold a place, as being compounds formed by the direct union of two elements; and in the former they are the roots or radicals of the various organic products. The following tabular view represents the composition of those which have as yet been studied.

	Hydrogen.	Carbon.	Equiv.	Formulae.
Light carburetted hydrogen	2 2 eq.+ 6.12	1 eq. = 8.12		H_2C
Olefiant gas . . .	2 2 eq.+12.24	2 eq. = 14.14		H_2C_2
Etherine . . .	4 4 eq.+24.48	4 eq. = 28.48		H_4C_4
Paraffine . . .	} Same ratio of elements as in etherine, but eq. is unknown.			
Eupione . . .				
Rose-oil-stearine . . .				
Wax-oil . . .				
Benzin or Bicarburet of hydrogen . . .	3 3 eq.+36.72	6 eq. = 39.72		H_3C_6
Naphtha . . .	5 3 eq.+36.72	6 eq. = 41.72		H_5C_6
Oil of turpentine . . .	} 8 8 eq.+ 61.2	10 eq. = 69.2		H_8C_{10}
Citrine . . .				
Camphire . . .				
Oil of Copaiva . . .				
Juniper oil . . .				
Lemon oil . . .				
Savin-tree oil . . .				
Black pepper oil . . .	} 4 4 eq.+61.2	10 eq. = 65.2		H_4C_{10}
Naphthaline . . .				
Paranaphthaline . . .				
Idrialine . . .	7 7 eq.+122.4	20 eq. = 129.4		H_7C_{20}

Light Carburetted Hydrogen.—*Effit.*—This gas is sometimes called *heavy inflammable air*, the *inflammable air of marshes*, and *hydrocarburet*. Agreeably to the principles of chemical nomenclature, taking carbon as the electro-negative element, it is a *carburet of hydrogen*; but it is generally termed *light carburetted hydrogen*. It is formed abundantly in stagnant pools during the spontaneous decomposition of dead vegetable matter; and it may readily be procured by stirring the mud at the bottom of them, and collecting the gas, as it escapes, in an inverted glass vessel. In this state it is found to contain 1-20th of carbonic acid gas, which may be removed by means of lime water or a solution of pure potassa, and 1-15th or 1-20th of nitrogen. This is the only convenient method of obtaining it.

Prop.—Colourless, tasteless, nearly inodorous; always gaseous when uncombined; does not change the colour of litmus or turmeric paper. Water, according to Henry, absorbs about 1-60th of its volume. It extinguishes all burning bodies, and is unable to support the respiration of animals. It is highly inflammable; and when a jet of it is set on fire, it burns with a yellow flame, and with a much stronger light than is occasioned by hydrogen gas. With a due proportion of atmospheric air or oxygen gas it forms a mixture which detonates powerfully with the electric spark, or by the contact of flame. The sole products of the explosion are water and carbonic acid.

Dalton first ascertained the real nature of light carburetted hydrogen; and it has since been particularly examined by Thomson, Davy, and Henry. When 100 measures are detonated with rather more than twice their volume of oxygen gas, the whole of the inflammable gas and precisely 200 measures of the oxygen disappear, water is condensed, and 100 measures of carbonic acid are produced. Now 100 measures of carbonic acid gas contain (page 293) 100 of carbon vapour and 100 of oxygen gas, just half the oxygen which had been employed; and the remaining oxygen requires 200 measures of hydrogen to form water. Hence, at 60° F. and 30 inches Bar.,

100	cubic inches of carbon vapour weigh	13.153	grains
200	do. hydrogen gas	4.2636	do.
100	do. light carburetted hydrogen must weigh	17.4166	do.

These weights are obviously in the ratio of 2 to 6.12, as already

assigned, and the sp. gr. of such a gas ought to be 0.5594, which is nearly the quantity found experimentally by Thomson and Henry. Light carburetted hydrogen is not decomposed by electricity, nor by being passed through red-hot tubes, unless the temperature is very intense, in which case some of the gas does suffer decomposition, each volume yielding two volumes of pure hydrogen gas and a deposit of charcoal. Mixed with chlorine, no action takes place at common temperatures, when quite dry, even if exposed to the direct solar rays. If moist, and the mixture is kept in a dark place, still no action ensues; but if light be admitted, particularly sunshine, decomposition follows. The nature of the products depends upon the proportion of the gases. If four measures of chlorine and one of light carburetted hydrogen are present, carbonic and hydrochloric acid gases will be produced: two volumes of chlorine combine with two volumes of hydrogen contained in the carburetted hydrogen, and the other two volumes of chlorine decompose so much water as will likewise give two volumes of hydrogen, forming hydrochloric acid; while the oxygen of the water unites with the carbon, and converts it into carbonic acid. If there are three instead of four volumes of chlorine, carbonic oxide will be generated instead of carbonic acid, because one-half less water will be decomposed (Henry). If a mixture of chlorine and light carburetted hydrogen is electrified or exposed to a red heat, hydrochloric acid is formed, and charcoal deposited.

Its eq. is 8.12; eq. vol. = 100; symb. H_2C .

It was first ascertained by Henry (Nicholson's Journal, vol. xix.); and his conclusions have been fully confirmed by the subsequent researches of Davy, that the *fire-damp* of coal-mines consists almost solely of light carburetted hydrogen. This gas often issues in large quantity from between beds of coal, and by collecting in mines, owing to deficient ventilation, gradually mingles with atmospheric air, and forms an explosive mixture. The first unprotected light which then approaches, sets fire to the whole mass, and an explosion ensues. These accidents, which were formerly so frequent and so fatal, are now comparatively rare, owing to the employment of the safety-lamp. For this invention we are indebted to Davy, who established the principles of its construction by a train of elaborate experiment and close reasoning, which may be regarded as one of the happiest efforts of his genius (Essay on Flame).

Davy commenced the inquiry by determining the best proportion of air and light carburetted hydrogen for forming an explosive mixture. When the inflammable gas is mixed with 8 or 4 times its volume of air, it does not explode at all. It detonates feebly when mixed with 5 or 6 times its bulk of air, and powerfully when 1 to 7 or 8 is the proportion. With 14 times its volume, it still forms a mixture which is explosive; but if a larger quantity of air be admitted, a taper burns in it only with an enlarged flame.

The temperature required for causing an explosion was next ascertained. It was found that the strongest explosive mixture may come in contact with iron or other solid bodies heated to redness, or even to whiteness, without detonating, provided they are not in a state of actual combustion; whereas the smallest point of flame, owing to its higher temperature, instantly causes an explosion.

The last important step in the inquiry was the observation that flame cannot pass through a narrow tube. This led to the discovery, that the power of tubes in preventing the transmission of flame is not necessarily connected with any particular length; and that a very short one will have the effect, provided its diameter is proportionally reduced. Thus, a piece of fine wire gauze, which may be regarded as an assemblage of short narrow tubes, is quite impermeable to flame; and consequently, if a common oil lamp be completely surrounded with a cage of such gauze, it may be introduced into an explosive atmosphere of fire-damp and air, without kindling the mixture. This simple contrivance, which is appropriately termed the *safety-lamp*, not only prevents explosion, but indicates the precise moment of danger. When the lamp is carried into an atmosphere charged with fire-damp, the flame begins to enlarge; and the mixture, if highly explosive, takes fire as soon as it has passed through the gauze, and burns on its inner surface, while the light in the centre of the lamp is extinguished. Whenever this appearance is observed, the miner must instantly withdraw; for though the flame should not be able to communicate with the explosive mixture on the outside of the lamp, as long as the texture of the gauze remains entire, yet the heat emitted during the combustion is so great, that the wire, if exposed to it for a few minutes, would suffer oxidation, and fall to pieces.

The peculiar operation of small tubes in obstructing the passage of flame admits of a very simple explanation. Flame is gaseous matter heated so intensely as to be luminous; and Davy has shown

that the temperature necessary for producing this effect is far higher than the white heat of solid bodies. Now, when flame comes in contact with the sides of very minute apertures, as when wire gauze is laid upon a burning jet of coal gas, it is deprived of so much heat that its temperature instantly falls below the degree at which gaseous matter is luminous; and consequently, though the gas itself passes freely through the interstices, and is still very hot, it is no longer incandescent. Nor does this take place when the wire is cold only; —the effect is equally certain at any degree of heat which the flame can communicate to it. For since the gauze has a large extent of surface, and from its metallic nature is a good conductor of heat, it loses heat with great rapidity. Its temperature, therefore, though it may be heated to whiteness, is always so far below that of flame, as to exert a cooling influence over the burning gas, and reduce its heat below the point at which it is incandescent.

These principles suggest the conditions under which Davy's lamp would cease to be safe. If a lamp with its gauze red-hot be exposed to a *current* of explosive mixture, the flame may possibly pass so rapidly as not to be cooled below the point of ignition, and in that case an accident might occur with a lamp which would be quite safe in a calm atmosphere. It has been lately shown by Messrs. Upton and Roberts, lamp manufacturers of this city, that flame may in this way be made to pass through the safety-lamp as commonly constructed; and I am satisfied, from having witnessed some of their experiments, that the observation is correct. This then may account for accidents in coal-mines where the safety-lamp is constantly employed. An obvious mode of avoiding such an evil is to diminish the apertures of the gauze; but this remedy is nearly impracticable from the obstacle which very fine gauze causes to the diffusion of light. A better method is to surround the common safety-lamp with a glass cylinder, allowing air to enter solely at the bottom of the lamp through wire gauze of extreme fineness, placed horizontally, and to escape at top by a similar contrivance. Upton and Roberts have constructed a lamp of this kind, through which I have in vain tried to cause the communication of flame, and which appears to me perfectly secure: should an accident break the glass, their lamp would be reduced to a safety-lamp of the common construction. Davy's lamp thus modified gives a much better light than without the glass, just as all lamps burn better with a shade than without one.

Olefiant Gas.—*Hydrocarbon*.—Discovered in 1796 by some associated Dutch chemists, who gave it the name of *bleijgas*, from its property of forming an oil-like liquid with chlorine. It is sometimes, but very improperly, called bicarburetted or percarburetted hydrogen. The ratio of its elements being as 1 to 1, suggests the term carburet of hydrogen; but this does not indicate that 2 eqs. of carbon are combined with 2 eqs. of hydrogen to form 1 eq. of the gas. Perhaps the expression $\frac{2}{1}$ carburet of hydrogen will adequately express this,—a principle of nomenclature already adopted by some of the German chemists.

Prep.—By mixing in a capacious retort one part by weight of absolute alcohol with four of concentrated sulphuric acid, and heating the mixture as soon as it is made. The acid soon acts upon the alcohol; effervescence ensues, and olefiant gas passes over. The chemical changes which take place are of a complicated nature, and the products numerous. At the commencement of the process, the olefiant gas is mixed only with a little ether; but in a short time the solution becomes dark, the formation of ether declines, and the odour of sulphurous acid begins to be perceptible: towards the close of the operation, though olefiant gas is still the chief product, sulphurous acid is freely disengaged, some carbonic acid is formed, and charcoal in large quantity deposited. The olefiant gas may be collected either over water or mercury. The greater part of the ether condenses spontaneously; and the sulphurous and carbonic acids may be separated by washing the gas with lime water, or a solution of pure potassa. The olefiant gas in this process is derived solely from the alcohol; the theory of its formation, as well as that of the accompanying products, will be given under the head Alcohol.

Prop.—Colourless, tasteless, inodorous; hitherto only known in a gaseous state. Water absorbs about one-eighth of its volume. Like the preceding compound, it extinguishes flame, is unable to support the respiration of animals, and is set on fire when a lighted candle is presented to it, burning slowly with the emission of a dense white light. With a proper quantity of oxygen gas, it forms a mixture which may be kindled by flame or the electric spark, and which explodes with great violence. To burn it completely, it should be detonated with four or five times its volume of oxygen. On conducting this experiment with the requisite care, Henry finds that for each measure of olefiant gas, precisely three of oxygen disappear, deposition of water takes place, and two measures of car-

basic acid are produced. From these data the proportion of its constituents may easily be deduced in the following manner:—Two measures of carbonic acid contain two measures of the vapour of carbon, which must have been present in the olefant gas, and two measures of oxygen. Of two-thirds of the oxygen which disappeared are thus accounted for; and the other third must have combined with hydrogen. But one measure of oxygen requires for forming water precisely two measures of hydrogen, which must likewise have been contained in the olefant gas. Hence, as

200 cubic inches of the vapour of carbon, which weigh	26.306
hydrogen gas, which weigh	4.263
200 cubic inches of olefant gas must weigh	30.569

These weights are in the ratio 12.24 or 2 equivalents of carbon to 2, or 2 eqs. of hydrogen, as in the table. The sp. gr. of a gas so constituted (page 230) should be 0.9810; whereas the density found experimentally by Saussure is 0.9852, by Henry 0.967, and by Thomson 0.97.

By a succession of electric sparks it is resolved into charcoal and hydrogen; and the latter of course occupies twice as much space as the gas from which it was derived. It is also decomposed by transmission through red-hot tubes of porcelain. The nature of the products varies with the temperature. By employing a very low degree of heat, it may probably be converted solely into carbon, and light carburetted hydrogen; and in this case no increase of volume can occur, because these two gases, for equal bulks, contain the same quantity of hydrogen. But if the temperature is high, then a great increase of volume takes place; a circumstance which indicates the evolution of free hydrogen, and consequently the total decomposition of some of the olefant gas.

Its eq. is 14.24; eq. vol. = 100; symb. $2H + 2C$, or H_2C_2 . Chlorine acts powerfully on olefant gas. When these gases are mixed together in the ratio of two measures of the former to one of the latter, they form a mixture which takes fire on the approach of flame, and which burns rapidly with formation of hydrochloric acid gas, and deposition of a large quantity of charcoal. But if the gases are allowed to remain at rest after being mixed together, a very different action ensues. The chlorine, instead of decomposing the olefant gas, enters into direct combination with it, and a yellow liquid like oil is generated. Wöhler has remarked its prop-

duction by the contact of olefiant gas with certain metallic chlorides, especially the perchloride of antimony. The other compounds, the composition of which was given at page 387, are described in the organic chemistry. They belong to this department not only as being products of the organic kingdom, but also on account of their atomic constitution; for whenever they are acted on by chlorine or any other dehydrodizing agents, one part of the hydrogen, which enters into their composition, is shown to be in a state of combination different from the rest. Thus evidence is obtained that these compounds, although composed of nothing but hydrogen and carbon, are not formed by the direct union of these elements, but that a portion of the hydrogen with the carbon forms a compound radical, which acts the part of an element and combines as such with the remainder of the hydrogen.

SECTION III.

COMPOUNDS OF HYDROGEN AND SULPHUR.

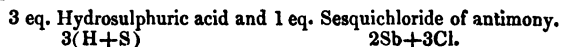
SULPHUR unites with hydrogen in at least two proportions, and the resulting compounds are thus constituted:—

	Hydrogen.	Sulphur.	Equiv.	Formulæ.
Hydrosulphuric acid .	1 1 eq. + 16·1	1 eq. = 17·1		HS.
Persulphuret of hydrogen	1 1 eq. + 32·2	2 eq. = 33·2		HS ₂ .

Hydrosulphuric Acid.—*Hist. and Prep.*—Commonly known under the name of sulphuretted hydrogen. It is best prepared by heating sesquisulphuret of antimony in a retort, or other convenient glass vessel, with four or five times its weight of strong hydrochloric acid; when, by an interchange of elements, sesquichloride of antimony and hydrosulphuric acid are generated, the latter of which escapes with effervescence. The elements concerned before and after the change, are



which yield



It may also be formed by the action of sulphuric acid diluted with 3 or 4 parts of water on protosulphuret of iron: this sulphuret and water interchange elements, hydrosulphuric acid and protoxide of iron are generated, and the latter unites with sulphuric acid, while

the former in the state of gas is rapidly disengaged. Hydrochloric acid may be substituted for the sulphuric. A sulphuret of iron may be procured for the purpose, either by igniting common iron pyrites, by which means nearly half of its sulphur is expelled, or by exposing to a low red heat a mixture of two parts of iron filings and rather more than one part of sulphur. The materials should be placed in a common earthen or cast-iron crucible, and be protected as much as possible from the air during the process. The sulphuret procured from iron filings and sulphur always contains some uncombined iron, and therefore the gas obtained from it is never quite pure, being mixed with a little free hydrogen. This, however, for many purposes, is immaterial.

Prop.—Colourless gas, which reddens moist litmus paper feebly, and is distinguished from all other gaseous substances by its offensive taste and odour, which is similar to that of putrefying eggs, or the water of sulphurous springs. Under a pressure of 17 atmospheres, at 50°, it is compressed into a limpid liquid, which resumes the gaseous state as soon as the pressure is removed. To animal life it is very injurious. According to Dupuytren and Thenard, the presence of 1-1500th of this gas in air is instantly fatal to a small bird; 1-1000th killed a middle-sized dog; and a horse died in an atmosphere which contained 1-250th of its volume.

It extinguishes all burning bodies; but the gas takes fire when a lighted candle is immersed in it, and burns with a pale blue flame. Water and sulphurous acid are the products of its combustion, and sulphur is deposited. With oxygen gas it forms a mixture which detonates by the application of flame or the electric spark: if 100 measures of it are exploded with 150 of oxygen, the former is completely consumed, the oxygen disappears, water is deposited, and 100 measures of sulphurous acid gas remain (Thomson). From the result of this experiment, the composition of hydrosulphuric acid gas may be inferred; for it is clear, from the composition of sulphurous acid (page 302), that two-thirds of the oxygen must have combined with sulphur; and, therefore, that the remaining one-third contributed to the formation of water. Consequently, hydrosulphuric acid contains its own volume of hydrogen gas, and 16·66 of the vapour of sulphur; and since

16·66 cubic inches of the vapour of Sulphur weigh	.	.	.	Grains.
100 cubic inches of Hydrogen gas weigh	.	.	.	34·361
				2·1318
100 cubic inches of Hydrosulp. acid gas must weigh	.	.	.	36·4928

The sp. gr. of a gas so constituted should be 1.1774, which agrees with observation; and its elements are in the ratio of 1 to 16.01, as already mentioned.

The accuracy of this view is confirmed by several circumstances. Thus, according to Gay-Lussac and Thenard, the weight of 100 cubic inches of hydrosulphuric acid gas is 36.33 grains. When sulphur is heated in hydrogen gas, hydrosulphuric acid is generated without any change of volume. On igniting platinum wires in it by means of the voltaic apparatus, sulphur is deposited, and an equal volume of pure hydrogen remains; and a similar effect is produced, though more slowly, by a succession of electric sparks (Elements of Davy, p. 282). Gay-Lussac and Thenard found that on heating tin in hydrosulphuric acid gas, sulphuret of tin is formed; and when potassium is heated in it, a vivid combustion ensues, with formation of sulphuret of potassium. In both cases, pure hydrogen is left, which occupies precisely the same space as the gas from which it was derived (Recherches Physico-Chimiques, vol. 1).

The salts of hydrosulphuric acid are called *hydrosulphates*, and sometimes *hydrosulphurets*. This acid, however, rarely unites directly with metallic oxides; but in most cases its hydrogen combines with the oxygen of the oxide and its sulphur with the metal. All the hydrosulphates which do exist are decomposed by sulphuric or hydrochloric acids, and hydrosulphuric acid gas is disengaged with effervescence.

Recently boiled water absorbs its own volume of hydrosulphuric acid, becomes thereby feebly acid, and acquires the peculiar odour and taste of sulphurous springs. The gas is expelled without change by boiling the water.

The elements of hydrosulphuric acid may easily be separated from one another. A solution of the gas cannot be preserved in an open vessel, because its hydrogen unites with the oxygen of the atmosphere, and sulphur is deposited. When mixed with sulphurous acid, both compounds are decomposed, water is generated, and sulphur set free. On pouring into a bottle of the gas a little fuming nitric acid, mutual decomposition ensues, a bluish-white flame frequently appears, sulphur and nitrous acid fumes come into view, and water is generated. Chlorine, iodine, and bromine decompose it, with separation of sulphur, and formation of hydrochloric, hydriodic, and hydrobromic acids. An atmosphere charged

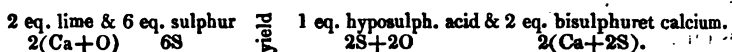
with hydrosulphuric acid gas may be purified by means of chlorine in the space of a few minutes.

Hydrosulphuric acid gas is readily distinguished from other gases by its odour; by tarnishing silver with which it forms a sulphuret, and by the character of the precipitate which it produces with solutions of arsenious acid, tartar emetic, and salts of lead. The most delicate test of its presence, when diffused in the air, is moist carbonate of oxide of lead spread on white paper.

Its eq. is 17.14; eq. vol. = 100; symb. HS.

Protosulphuret of Hydrogen.—*Hist. and Prep.*—Discovered by Schaeple, but first specially described by Berthollet (*Ann. de Chimie*, *lxxv*). When protosulphuret of potassium (or of any metal of the alkalies and alkaline earths) is mixed in solution with sulphuric acid, the oxygen of water unites with potassium and its hydrogen with sulphur, just as when protosulphuret of iron is employed, hydrosulphuric acid and sulphate of potassa being generated: the elements $K + S$ and $H + O$ mutually interchange, and yield $K + O$ and $H + S$. If the potassium be combined with two or more equivalents of sulphur as in the so called *liver of sulphur* made by fusing carbonate of potassa with half of its weight of sulphur, then one of two events will happen: the hydrogen of the decomposed water will either unite with 1 eq. of sulphur and form hydrosulphuric acid; the superfluous sulphur subsiding in the form of a grey hydrate, or with 2 eqs. of sulphur, and give rise to persulphuret of hydrogen. Now, the former of these changes always occurs when the acid is added to the persulphuret of potassium; and the latter takes place when a concentrated solution of that sulphuret is added by little and little to the acid, provided the acid is in considerable excess, and the mixture well stirred after each addition. The same phenomena ensue when hydrochloric instead of sulphuric acid is employed; but then there are two sources from which hydrogen may be supplied. It may be derived, as above, from decomposed water, hydrochlorate of potassa been generated; or hydrochloric acid itself may be decomposed, its hydrogen uniting with sulphur and its chlorine with potassium. On all such occasions I adopt the latter view, and will give reasons for doing so in the section introductory to the study of the metals. Such are the principles to be attended to in preparing persulphuret of hydrogen. In practice it is conveniently made by boiling equal parts of recently slaked lime and flowers of sulphur with

5 or 6 parts of water for half an hour, when a deep orange-yellow solution is formed, which contains persulphuret of calcium. Let this liquid be filtered, and gradually added cold to an excess of hydrochloric acid diluted with about twice its weight of water, briskly stirring. A copious deposit of sulphur falls (the sulphur præcipitatum of the London Pharmacopœia), and persulphuret of hydrogen gradually subsides in the form of a yellowish semi-fluid matter like oil. The change which ensues in the formation of the yellow solution may be theoretically represented thus:—



The hyposulphurous acid exists in solution united with lime, and is decomposed when hydrochloric acid is added, resolving itself into sulphurous acid and sulphur (page 307); a change not essentially connected with the production of persulphuret of hydrogen, but resulting from the mode of preparing the persulphuret of calcium. It is probable that the calcium is combined with more than 2 eqs. of sulphur, and that the deposited sulphur is derived from that source as well as from decomposed hyposulphurous acid.

Prop.—From the facility with which this substance resolves itself into sulphur and hydrosulphuric acid, its history is imperfect: we are indebted to an essay by Thenard for the principal facts which are known (*An. de Ch. et Ph.* xlviii. 79). At common temperatures it is a viscid liquid, of a yellow colour, with a density of about 1.769, and a consistence varying between that of a volatile and fixed oil. It has the peculiar odour and taste of hydrosulphuric acid, though in a less degree. Its elements are so feebly united, that in the cold it gradually resolves itself into sulphur and hydrosulphuric acid, and suffers the same change instantly by a heat considerably short of 212° F. Decomposition is also produced by the contact of most substances, especially of metals, metallic oxides, even the alkalies, and metallic sulphurets. Thus effervescence from the escape of hydrosulphuric acid gas is produced by peroxide of manganese, silica, the alkaline earths in powder, and solutions of potassa or soda; and the oxides of gold and silver are reduced by it with such energy, that they are rendered incandescent. It is remarkable that the substance which causes the decomposition often undergoes no chemical change whatever. In these respects persulphuret of hydrogen bears a close analogy to peroxide of hydrogen; and Thenard has traced other

points of resemblance. They are both, for instance, rendered more stable by the presence of acids; they both whiten the tongue and skin when applied to them, and they are both possessed of bleaching properties.

The composition of persulphuret of hydrogen has been variously stated. According to Dalton it is a bisulphuret, consisting of two equivalents of sulphur and one of hydrogen; and this view of its composition is corroborated by Sir John Herschel's analysis of persulphuret of calcium (Edin. Phil. Journal, i. 13). But Thenard found its constituents to vary; whence it is probable that hydrogen is capable of uniting with sulphur in several proportions.

Persulphuret of hydrogen is sometimes regarded as an acid; and on this supposition it may be termed *hydropersulphuric acid*, and its salts *hydropersulphates*. This view is founded on the hypothesis, that the solutions formed by boiling lime or an alkali with sulphur contain hyposulphite and hydropersulphate of lime, the hydrogen in the one acid and oxygen in the other being attributed to decomposed water, and not hyposulphite of lime and persulphuret of calcium, as I have supposed. The latter view is more consistent with the fact that persulphuret of hydrogen in its free state has no acidity, and exhibits no tendency to unite with alkalis.

Its eq. is = 33.2; symb. H S_2 .

SECTION IV.

HYDROGEN AND SELENIUM.—HYDROSELENIC ACID.

SELENIUM, like sulphur, forms a gaseous compound with hydrogen, which has distinct acid properties, and is termed *seleniuretted hydrogen*, or *hydroselenic acid*. It is disengaged by the action of dilute sulphuric or hydrochloric acid on a protoseleniuret of any of the more oxidable metals, such as potassium, calcium, manganese, or iron, the explanation being the same as in the formation of hydrosulphuric acid from protosulphuret of iron.

Hydroselenic acid gas is colourless. Its odour is at first similar to that of hydrosulphuric acid; but it afterwards irritates the lining membrane of the nose powerfully, excites catarrhal symptoms, and destroys for some hours the sense of smelling. It is absorbed freely by water, forming a colourless solution, which reddens litmus paper, and gives a brown stain to the skin. The

acid is soon decomposed by exposure to the atmosphere; for the oxygen of the air unites with the hydrogen of the hydroselenic acid, and selenium, in the form of a red powder, subsides. It is decomposed by nitric acid and chlorine in the same manner as hydrosulphuric acid; and, like that gas, it decomposes many metallic salts, the hydrogen of the acid combining with the oxygen of the oxide, while an insoluble seleniuret of the metal is generated.

According to the analysis of Berzelius, hydroselenic acid consists of 89.6 parts or 1 eq. of selenium, and 1 part or 1 eq. of hydrogen: so that its eq. is 40.6; its symb. HSe.

SECTION V.

COMPOUNDS OF HYDROGEN AND PHOSPHORUS.

THE existence of two compounds of phosphorus and hydrogen, the phosphuretted and perphosphuretted hydrogen, have, until lately, been generally admitted by chemists. Their composition and properties have been closely studied by Dumas, Buff, Rose, and Graham (*An. de Ch. et Ph.* xxxi. 113; xli. 220; and xli. 5. *Phil. Mag.* v. 401.) The investigations of these chemists concurred in proving that phosphuretted hydrogen consists of 31.4 parts or 2 eqs. of phosphorus, and 3 parts or 3 eqs. of hydrogen; while the discordancy in their analyses of perphosphuretted hydrogen caused great uncertainty respecting its constitution. Thus, although Dumas and Rose agree that 100 measures of perphosphuretted hydrogen contains 150 measures of hydrogen, the former states that 1 part of hydrogen is united with 15.9 of phosphorus, the latter with 10.52, while Thomson estimates the quantity at 12. The result of Rose would indicate that the two compounds of phosphorus and hydrogen are isomeric, being identical in composition, and differing in character only by the one being spontaneously inflammable, and the other not so. The accuracy of the analytical results of Rose have been recently established by the discoveries of Leverrier (*An. de Ch. et Ph.* lx. 174), who has proved that perphosphuretted hydrogen is a mixture of phosphuretted hydrogen with about $\frac{1}{3}$ of its volume of a spontaneously inflammable compound, which he considers to be composed of 31.4 parts or 2 eqs. of phosphorus, and 2 parts or 2 eqs. of hydrogen. In the same paper he establishes the existence of a compound

formed of 31·4 parts or 2 eqs. of phosphorus, and 1 part or 1 eq. of hydrogen. The compounds of phosphorus and hydrogen are therefore,

	Phos.	Hyd.	Equiv.	Formulae.
Solid Phosphuretted Hydrogen	. 31·4 2 eq. +	1 1 eq. =	32·4	P_2H
Inflammable ditto	. 31·4 2 eq. +	2 2 eq. =	33·4	P_2H_2
Gaseous ditto	. 31·4 2 eq. +	3 3 eq. =	34·4	P_2H_3

Solid Phosphuretted Hydrogen.—When phosphuretted hydrogen gas, recently prepared by the action of quick-lime and phosphorus, is exposed in the moist state to a strong diffused light, or to the direct rays of the sun, the solid phosphuretted hydrogen is deposited on the sides of the glass vessel. It is also left as an insoluble powder when phosphuret of potassium is dissolved in water. As obtained by the former process, it is a canary yellow flocculent matter, is insoluble in water and alcohol; but with the former, a slow oxidation takes place, and hydrogen is evolved. It is not altered by a temperature of 234° , but heated beyond that point it is decomposed. When brought into contact with chlorine and nitric acid, it suffers instantaneous decomposition. According to the analysis of Leverrier, it is composed of 1 part or 1 eq. of hydrogen, and 31·4 parts or 2 eqs. of phosphorus. Hence its eq. is 32·4; symb. HPh_2 .

PHOSPHURETTED HYDROGEN.

Hist. and Prep.—Discovered by Davy in 1812. It may be prepared by several methods. Davy prepared it by heating hydrated phosphorous acid in a retort (page 314); and it is evolved from hydrous hypophosphorous acid by similar treatment, and by the action of strong hydrochloric acid on phosphuret of calcium according to Dumas. It may also be obtained, but in an impure state, by boiling phosphorus with a solution of potassa or milk of lime. Its production is in these cases dependent on the decomposition of water, the oxygen and hydrogen of which unites with different portions of phosphorus, and phosphoric acid, hypophosphorous acid and phosphuretted hydrogen are generated.

Prop.—A transparent colourless gas, of an exceedingly offensive odour and bitter taste. It has no action on test paper. It is absorbed in small quantity by water, but freely by solutions of chloride of calcium or sulphate of the oxide of copper, by which means its purity may be ascertained. Like sulphuretted hydrogen, it frequently decomposes metallic salts, giving rise to the formation of water and a phosphuret of the metal. But if the metal have a

feeble affinity for oxygen, it is thrown down in the metallic state, and water and phosphoric acid are generated. This is the case, according to Rose, with solutions of gold and silver.

It is a non-supporter of combustion, and is very destructive to animal life. When pure, it may be mixed with air or oxygen gas at common temperatures without danger; but the mixture detonates with the electric spark, or at a temperature of 300° . Even diminished pressure causes an explosion; an effect which, in operating with a mercurial trough, is produced simply by raising the tube, so that the level of the mercury within may be a few inches higher than at the outside. Such is the property of the pure gas, as obtained from the hydrated phosphorous or hypophosphorous acids; but if it be procured from the action of phosphorus on potassa or hydrate of lime, it is remarkable for being spontaneously inflammable when mixed with air or oxygen gas. If the beak of the retort from which it issues is plunged under water, so that successive bubbles of the gas may arise through the liquid, a very beautiful appearance takes place. Each bubble, on reaching the surface of the water, bursts into flame, and forms a ring of dense white smoke, which enlarges as it ascends, and retains its shape, if the air is tranquil, until it disappears. The wreath is formed by the products of the combustion—metaphosphoric acid and water. If received in a vessel of oxygen gas, the entrance of each bubble is instantly followed by a strong concussion, and a flash of white light of extreme intensity. It is remarkable that whatever may be the excess of oxygen, traces of phosphorus always escape combustion; but that if the gas be previously mixed with three times its volume of carbonic acid, and be then mixed with oxygen, the combustion is perfect. Dalton observed that it may be mixed with pure oxygen in a tube three-tenths of an inch in diameter without taking fire; but that the mixture detonates when an electric spark is transmitted through it.

In consequence of the combustibility of phosphuretted hydrogen, it would be hazardous to mix it in any quantity with air or oxygen gas in close vessels. For the same reason care is necessary in the formation of this gas, lest, in mixing with the air of the apparatus, an explosion ensue, and the vessel burst. The risk of such an accident is avoided, when phosphuret of calcium is used, by filling the flask or retort entirely with dilute acid; and in either of the other processes, by causing the phosphuretted hydrogen to be formed

slowly at first, in order that the oxygen gas within the apparatus may be gradually consumed. A very simple method of averting all danger has been mentioned by Graham. It consists in moistening the interior of the retort with one or two drops of ether, the vapour of which, when mixed with atmospheric air even in small proportion, effectually prevents the combustion of phosphuretted hydrogen. The same effect may be produced by the addition of several other bodies. He also finds that a gas, which is not spontaneously inflammable, acquires this property on being mixed with from $\frac{1}{1000}$ to $\frac{1}{10000}$ of its volume of nitrous acid. According to Leverrier, it is very probable that there exists a compound of phosphorus and hydrogen composed of 2 eqs. of each of its elements, and that this compound being spontaneously inflammable communicates that property to phosphuretted hydrogen gas. This opinion is grounded on the fact that when spontaneously inflammable phosphuretted hydrogen is kept for any length of time in a dark place it suffers no change, but if brought into a strong light solid phosphuretted hydrogen is deposited, and the residual gas is no longer spontaneously inflammable. Thus it appears that by the action of light P_2H_2 is decomposed, and P_2H and P_2H_3 are formed. The result of his analysis supports this view.

Dumas ascertained the composition of phosphuretted hydrogen by introducing into a tube containing the gas a fragment of bichloride of mercury, and applying heat so as to convert it into vapour. Mutual decomposition instantly took place: phosphuret of mercury and hydrochloric acid were generated; and 100 measures of gas, thus decomposed, yielded 300 measures of hydrochloric acid gas, corresponding to 150 of hydrogen. The quantity of hydrogen contained in any given volume of phosphuretted hydrogen is thus found; and the weight of the former deducted from that of the latter gives the quantity of combined phosphorus. This inference is conformable to the quantity of oxygen required for the combustion of phosphuretted hydrogen. Thomson affirms that when this gas is detonated with 1.5 of its volume of oxygen gas, the only products are water and phosphorous acid; but that when the oxygen is in considerable excess, two volumes disappear for one of the compound, and water and phosphoric acid are generated. Now the hydrogen contained in one volume of phosphuretted hydrogen is equal to 1.5, and it unites with 0.75 of oxygen. Hence if 0.75, or $\frac{3}{4}$, be deducted from 1.5 and from 2, the remainders, $\frac{3}{4}$ and $\frac{1}{4}$,

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represent the relative quantity of oxygen which is required to convert the same weight of phosphorus into phosphorous and phosphoric acid. These numbers are obviously in the ratio of 3 to 5, as already stated on the authority of Berzelius (page 312). The elements of the calculation have been confirmed both by Dumas and Buff.

Agreeably to these views, and to the combining volume of phosphorus (page 231), 100 measures of phosphuretted hydrogen gas contain 150 of hydrogen gas and 25 of the vapour of phosphorus; and hence, as

							Grains.
150	cubic inches of Hydrogen gas weigh	.	:	:	:	.	3.1977
25	do. Phosphorous vapour weigh	.	:	:	:	.	33.5425
100	do. Phosphuretted Hydrogen gas should weigh	36.7402.

The calculated density of a gas so constituted should be 1.1853, which is nearly a mean of the observations of Dumas and Rose.

If the equivalent of phosphorus were 31.4 instead of 15.7, as is very far from improbable, then the combining volume of phosphorous vapour would be 50 instead of 25 (page 231); and phosphuretted hydrogen would consist of 50 measures of phosphorous vapour and 150 of hydrogen gas condensed into 100 measures, thus agreeing in composition with ammoniacal gas.

Phosphuretted hydrogen has neither an acid nor alkaline reaction; but in its chemical relations it inclines to alkalinity. Thus it unites with hydrobromic and hydriodic acids, forming definite compounds which crystallize in cubes; and Rose finds that it unites with metallic chlorides, forming compounds analogous to those which ammonia forms with metallic chlorides.

Its eq. is 34.4; eq. vol. = 100; symb. $2P + 3H$, or P_2H_3 .

SECTION VI.

COMPOUNDS OF NITROGEN AND CARBON.

BICARBURET OF NITROGEN, OR CYANOGEN GAS.

Hist. and Prep.—Discovered in 1815 by Gay-Lussac (An. de Ch. xcv.). It is prepared by heating carefully dried bicianuret of mercury in a small glass retort by means of a spirit lamp. This cyanuret, which was formerly considered a compound of oxide of

mercury and prussic acid, and was then called *prussiate of mercury*, is composed of metallic mercury and cyanogen. On exposure to a low red heat it is resolved into its elements; the cyanogen passes over in the form of gas, and the metallic mercury is sublimed. The retort, at the close of the process, contains a small residue of a dark brown matter like charcoal, but which Johnston has shown to consist of the same ingredients as the gas itself.

Prop.—A colourless gas possessing a strong pungent and very peculiar odour. At the temperature of 45° and under a pressure of 3.6 atmospheres, it is a limpid liquid, which Kemp finds to be a non-conductor of electricity, and which resumes the gaseous form when the pressure is removed. It extinguishes burning bodies; but it is inflammable, and burns with a beautiful and characteristic purple flame. It can support a strong heat without decomposition. Water at the temperature of 60° absorbs 4.5 times, and alcohol 23 times its volume of the gas. The aqueous solution reddens litmus paper; but this effect is not to be ascribed to the gas itself, but to the presence of acids which are generated by the mutual decomposition of cyanogen and water. It appears from the observations of Wöhler that two of the products are cyanic acid and ammonia; which, uniting together, generate urea (*An. de Ch. et Ph.* xliii. 73).

The composition of cyanogen may be determined by mixing that gas with a due proportion of oxygen, and inflaming the mixture by electricity. Gay-Lussac ascertained in this way that 100 measures of cyanogen require 200 of oxygen for complete combustion, that no water is formed, and that the products are 200 measures of carbonic acid gas and 100 of nitrogen. Hence it follows that cyanogen contains its own bulk of nitrogen, and twice its volume of the vapour of carbon. Consequently, since

100 cubic inches of Nitrogen gas weigh	Grains.
200 do. the vapour of Carbon weigh	30.166
100 cubic inches of Cyanogen gas must weigh	56.472
The ratio of its elements by weight is,					
Nitrogen	.	30.166	.	0.9727	14.15 1 eq.
Carbon	.	26.306	.	0.8430 (2+0.4215)	12.24 2 eq.

The sp. gr. of a gas so constituted is $0.9727 + 0.843 = 1.8157$, which is near 1.8064, the number found experimentally by Gay-Lussac.

Cyanogen is a *bicarburet of nitrogen*, the formula of which is

$N + 2C$, or NC_2 ; but its most convenient name is *cyanogen*, proposed by its discoverer,* which may be expressed shortly by *Cy*. Its eq. is 26·89.

Paracyanogen.—An examination of the brown matter, left in the retort after the preparation of cyanogen gas, has been made by Johnston, who by burning it with chlorate of potassa found it to contain carbon and nitrogen united in the same ratio as in cyanogen gas. It is, in fact, a solid bicarburet of nitrogen, isomeric with cyanogen, but differing from it essentially in its physical and chemical relations. On heating this solid bicarburet in the open air, several definite compounds of carbon and nitrogen may be successively obtained. After considerable heating, the ratio of carbon to nitrogen is as 3 to 2; again heated, the proportion becomes as 7 to 6; and finally, after a still longer heat, the ratio of the equivalents is as 1 to 1. Thus the carbon is gradually burned away, leaving the nitrogen fixed, until a protocarburet of nitrogen is formed. On continuing the heat after this period, both elements fly off together, and the whole is dissipated. The solid bicarburet of cyanogen is also generated, when a saturated solution of cyanogen in alcohol is kept in contact with mercury; and Johnston suggests that the carbonaceous residue after the charring of animal substances by heat, is probably in many cases a carburet of nitrogen, and not pure charcoal as is commonly thought. (Brewster's Journ. N.S. i. 75.) Paracyanogen is soluble in sulphuric and nitric acids, and forms a compound with oxygen in which 1 eq. of oxygen is combined with 4 eqs. of nitrogen and 8 eqs. of carbon. Hence the eq. of paracyanogen is probably 105·56, and its symb. N_4C_8 .

Mellon.—Is obtained when sulphuret of cyanogen, melams, melamins, ammelins, or ammelids, is exposed to a red heat. It is a lemon yellow powder, is insoluble in water and alcohol, but is dissolved and decomposed by acids and alkalies. Exposed to a strong red heat, it is decomposed and forms 1 vol. of nitrogen and 3 vols. of cyanogen gas. It is one of the compound radicals. Its eq. is 93·32; symb. N_4C_6 . (*Lieb. An.* ix. 5.)

Cyanogen, though a compound body, has a remarkable tendency to combine with elementary substances. Thus it is capable of uniting with the simple non-metallic bodies, and evinces a strong attraction for metals. When potassium, for instance, is heated in

* From *κύανος*, blue, and *γεννάω*, I generate; because it is an essential ingredient of Prussian blue.

cyanogen gas, such energetic action ensues, that the metal becomes incandescent, and cyanuret of potassium is generated. The affinity of cyanogen for metallic oxides, on the contrary, is comparatively feeble. It enters into direct combination with a few alkaline bases only, and these compounds are by no means permanent. From these remarks it is apparent that cyanogen has no claim to be regarded as an acid, as it has none of the properties of a compound: It is, in fact, a compound radical of organic chemistry, and therefore its various combinations will be described in that part of the work.

SECTION VII.

COMPOUND OF PHOSPHORUS AND NITROGEN.

Phosphuret of Nitrogen.—First described by Rose (Pogg. An. xxviii. 529). On saturating either of the chlorides of phosphorus with dry ammoniacal gas, a white solid mass is obtained, which on exposure to a strong red heat gives rise to the formation of phosphuret of nitrogen, hydrochloric acid gas being at the same time evolved. It is also formed when the vapour of either chlorides of phosphorus are brought into contact with sal-ammonia heated nearly to its point of sublimation.

It is a light snow-white powder; is insoluble in water, and in dilute acid, or alkaline solutions. It is not changed by a red heat in close vessels, or in an atmosphere of chlorine, or the vapour of sulphur; but in hydrogen it is decomposed with the formation of ammoniacal gas. It is composed of 31·4 parts or 2 eqs. of phosphorus, and 14·15 parts or 1 eq. of nitrogen.

Its eq. is 45·55; symb. $N + 2P$, or NP_2 .

SECTION VIII.

COMPOUND OF SULPHUR, CARBON, ETC.

The compounds described in this section are thus constituted:

Bisulph. of Carbon	Carb. 6·12 + Sulp. 32·2=38·32.	$C + 2S CS_2$.
Sulph. of Phosphorus	Composition uncertain.	
Bisulph. of Selenium	Selen. 39·6 + Sulp. 32·2=71·8.	$Se + 2S SeS_2$.
Seleni. of Phosphorus	Composition uncertain.	

Bisulphuret of Carbon.—*Hist.*—This substance was discovered accidentally in the year 1796 by Professor Lampadius, who regard-

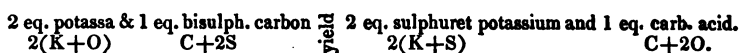
ed it as a compound of sulphur and hydrogen, and termed it *alcohol of sulphur*. Clément and Desormes first declared it to be a sulphuret of carbon, and their statement was fully confirmed by the joint researches of Berzelius and the late Dr. Marcet (Phil. Trans. 1813).

Prep.—Bisulphuret of carbon may be obtained by heating in close vessels native bisulphuret of iron (iron pyrites) with one-fifth of its weight of well-dried charcoal; or by transmitting the vapour of sulphur over fragments of charcoal heated to redness in a tube of porcelain. The compound, as it is formed, should be conducted by means of a glass tube into cold water, at the bottom of which it is collected. To free it from moisture and adhering sulphur, it should be distilled at a low temperature in contact with chloride of calcium.

Prop.—It is a transparent colourless liquid, which is remarkable for its high refractive power. Its sp. gr. is 1.272; of its vapour, 2.668. It has an acid, pungent, and somewhat aromatic taste, and a very fetid odour. It is exceedingly volatile; its vapour at 63.5° supports a column of mercury 7.36 inches long; and at 110° it enters into brisk ebullition. From its great volatility it may be employed for producing intense cold. It is very inflammable, and kindles in the open air at a temperature scarcely exceeding that at which mercury boils. It burns with a pale blue flame. Admitted into a vessel of oxygen gas, so much vapour rises as to form an explosive mixture; and when mixed in like manner with binocide of nitrogen, it forms a combustible mixture, which is kindled on the approach of a lighted taper, and burns rapidly, with a large greenish-white flame of dazzling brilliancy. It dissolves readily in alcohol and ether, and is precipitated from the solution by water. It dissolves sulphur, phosphorus, and iodine, and the solution of the latter has a beautiful pink colour. Chlorine decomposes it, with formation of chloride of sulphur. The pure acids have little action upon it. By nitro-hydrochloric acid it is changed into a white crystalline substance like camphor, which Berzelius regards as a compound of the hydrochloric, carbonic, and sulphurous acids.

Bisulphuret of carbon is a sulphur-acid, that is, unites with *sulphur-bases* to constitute compounds analogous to ordinary salts, and hence called *sulphur-salts*. Thus bisulphuret of carbon unites with sulphuret of potassium, forming a sulphur-salt, in which the former acts as an acid and the latter as a base. The same com-

pound is formed by the action of bisulphuret of carbon on a solution of pure potassa : but in this case sulphuret of potassium is first generated by an interchange of elements with a portion of bisulphuret of carbon, carbonic acid being produced at the same time. Thus



If the bisulphuret of carbon is in sufficient quantity, carbonic acid gas is disengaged, and a neutral compound results. Such is inferred to be the nature of the change, agreeably to the researches of Berzelius on the sulphur-salts.

Its eq. is 38·32 ; eq. vol. = 100 ; symb. CS₂.

Sulphuret of Phosphorus.—When sulphur and fused phosphorus are brought into contact they unite readily, but in proportions which have not been precisely determined ; and they frequently react on each other with such violence as to cause an explosion. For this reason the experiment should be made with a quantity of phosphorus not exceeding 30 or 40 grains. The phosphorus is placed in a glass tube, 5 or 6 inches long, and about half an inch wide ; and when by a gentle heat it is liquefied, the sulphur is added in successive small portions. Heat is evolved at the moment of combination, and hydrosulphuric and phosphoric acids, owing to the presence of moisture, are generated. This compound may also be made by agitating flowers of sulphur with fused phosphorus under water. The temperature should not exceed 160° ; for otherwise hydrosulphuric and phosphoric acids would be evolved so freely as to prove dangerous, or at least to interfere with the success of the process.

Sulphuret of phosphorus, from the nature of its elements, is highly combustible. It is much more fusible than phosphorus. A compound made by Faraday with about 5 parts of sulphur and 7 of phosphorus, was quite fluid at 32°, and did not solidify at 20° (Quarterly Journal, iv.).

Bisulphuret of Selenium.—Sulphur and selenium mix together in all proportions by fusion, and therefore by such means it is difficult to procure a definite compound ; but the bisulphuret of an orange colour was formed by Berzelius by precipitating a solution of selenious acid with hydrosulphuric acid. The sulphuret found by Stromeyer among the volcanic products of the Lipari isles is probably similar in composition. Bisulphuret of selenium fuses at

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a heat a little above 212° , and at a higher temperature may be sublimed without change. In the open air it takes fire when heated, and sulphurous, selenious, and selenic acids are the products of its combustion. The alkalies and soluble metallic sulphurets dissolve it. Nitric acid acts upon it with difficulty; but the nitro-hydrochloric converts it into sulphuric and selenious acids. (An. of Phil. xiv.)

Seleniuret of Phosphorus.—This compound may be prepared in the same manner as the sulphuret of phosphorus; but as selenium is capable of uniting with phosphorus in several proportions, the compound formed by fusing them together can hardly be supposed to be of a definite nature. This seleniuret is very fusible, sublimes without change in close vessels, and is inflammable. It decomposes water gradually when digested in it, giving rise to seleniuretted hydrogen, and one of the acids of phosphorus.

Sulphuret of Nitrogen.—This compound was formed by Gregory by the reaction of chloride of sulphur on a solution of ammonia. It is a colourless powder, insoluble in water, but dissolves in alcohol, and may thus be obtained in small crystals. It is characterized by its alcoholic solution forming with potassa a fine purple colour, which disappears shortly after, when the solution is found to contain hyposulphurous acid and ammonia. It contains from 92 to 93 per cent. of sulphur, and 7 to 8 of nitrogen.

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